Complexes of 1, 8-naphthyridines with elements of the first transition series
by Ahmad Emad

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in . CHEMISTRY
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Abstract:
Twenty-three new complexes of 1,8-naphthyridine (NN) and 2,7-dimethyl-1,8-naphthyridine (dmNN) with transition metals have been prepared and characterized. These complexes have been classified according to the anion for purposes of discussion.

Five halide complexes, four with copper(II) and one cobalt(II) complex with NN or dmNN were synthesized. Among these, two magnetically anomalous complexes, Cu(NN)Cl2 and Cu(NN)Br2 , were discovered. The possible structural geometries have been discussed.

Transition metal complexes of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), and sliver(I) perchlorates with NN were isolated. Chelation of NN with the divalent metal ions and monodentate coordination with silver(I) ion has been suggested.

Eight nitrate complexes of NN with the same transition elements have been prepared. Coordination of the naphthyridine molecule was found to be similar to that of the perchlorate compounds. In several of these complexes, coordination of the nitrate ions or water molecules is indicated by the infrared spectra.

The chemistry of complexes of this ligand with copper(I) ion was also studied. Four copper(I) complexes containing chloride and perchlorate anions with NN and dmNN were prepared. The possible coordination of the ligands and complexes is discussed and tentative structures proposed.

COMPLEXES OF 1,8-NAPHTHYRIDINES WITH ELEMENTS OF THE FIRST TRANSITION SERIES

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ABSTRACT

Twenty-three new complexes of 1,8-naphthyridine (NN) and 2,7-dimethyl-1,8-naphthyridine (dmNN) with transition metals have been prepared and characterized. These complexes have been classified according to the anion for purposes of discussion.

Five halide complexes, four with copper(II) and one cobalt(II) complex with NN or dmNN were synthesized. Among these, two magnetically anomalous complexes, $Cu(NN)Cl_2$ and $Cu(NN)Br_2$, were discovered. The possible structural geometries have been discussed.

Transition metal complexes of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), and silver(I) perchlorates with NN were isolated. Chelation of NN with the divalent metal ions and monodentate coordination with silver(I) ion has been suggested.

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INTRODUCTION

REVIEW OF LITERATURE:

In recent years, there has been some interest in transition metal complexes of heterocyclic molecules, containing two nitrogen atoms, forming four-membered ring chelates (1,2,3). Most of the common chelating agents form five- or six-membered rings and little is known about the chelating powers of agents forming four-membered rings. The nitrogen heterocycles able to form five-membered ring chelates have long been studied (4,5,6). The examples of these are: 2,2'-bipyridine, 1,10-phenanthroline, and their derivatives. These molecules are good π-bonding ligands and their strong crystal field properties are partially due to their ability to participate in π-bonding with the metal atoms (7). The compound 1,8-naphthyridine and its derivatives by comparison form four-membered ring chelates rather than five. Ionic ligands which form four-membered chelate rings have been known for a long time, and their complexes are stabilized by ionic charges. Examples of these are: perchlorates (8,9), nitrates (10), carbonates (11), and carboxylates (12). The similarity of chelated 1,8-naphthyridine complexes to chelate complexes of acetate ions suggests that naphthyridines might form polynuclear complexes with copper or other transition metals, as acetate does in a few cases.

Among these anionic ligands, the carboxylate ions have been most thoroughly studied. They may coordinate through one or both

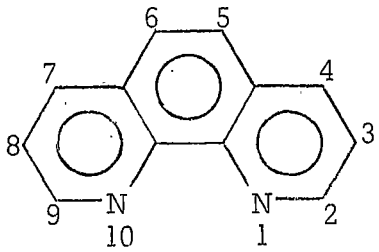
oxygens and they also form a class of polynuclear molecules with metal-metal interactions where the carboxylate group coordinates as a bidentate ligand to two metal atoms. A large number of these complexes have been investigated and characterized with copper(II) ions (12).

Dimeric copper(II) carboxylates show unusual magnetic properties. They exhibit a magnetic moment less than 1.7 B.M. compared with the value of 1.8-2.2 B.M. for normal copper(II) compounds. The magnetic susceptibility of these complexes does not obey the Curie-Weiss law. It passes through a maximum at or near room temperature and decreases rapidly as the temperature is lowered. Some of these compounds have anomalous magnetic properties at low temperature, but appear to be normal at or near room temperature. The interaction between d orbitals of copper(II) ions and the nature of the ligands are responsible for the magnitude of this subnormal behavior. The large overlap of the 3d orbitals between the copper(II) ions in the complex as well as the high tendency of the ligand for coordination will stabilize the dimeric structure of the complex. Similarly the formation of the dimeric compound in organic solvents such as alcohol, ether, etc. is more favorable than in aqueous solution. The dimeric structure is destroyed in water, resulting in monomeric hydrated ions. This is due to the stronger coordination ability of water compared with that of organic molecules.

1,8-NAPHTHYRIDINES AND THEIR COMPLEXES:— The compound 1,8-naphthyridine is an aromatic molecule (Fig. 1) having one unshared pair of electrons on each nitrogen and is symbolized throughout this thesis as "NN" for simplicity. In naphthyridine molecules the pairs of electrons in the nonbonding atomic orbitals of the nitrogens are responsible for their basic properties, since overlap of this orbital, as a Lewis base, with an orbital of a Lewis acid will result in a bond. Substitution of two methyl groups in 1,8-naphthyridine "dmNN" would be expected to increase the basicity of the substituted molecule as is observed in 1,10-phenanthroline. The basicity of the parent phenanthroline molecule is lower compared to the 2,9-dimethyl substituted derivative. The pK_a values for some of the nitrogen heterocycles are listed in Table I, but the value of pK_a for 1,8-naphthyridine has not been reported in the literature. In Table I, the pK_a values of different aromatic amines are compared in which the K_a values are the dissociation constants of protonated ammonium ions at 25°C in water.

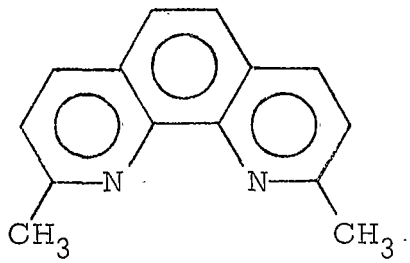
Table I

Compound	pK_a	Ref.
1,10-phenanthroline	4.86	(13)
2,9-dimethyl-1,10-phenanthroline	6.17	(13)
2,7-dimethyl-1,8-naphthyridine	4.50	(13)
Pyridine	5.18	(14)



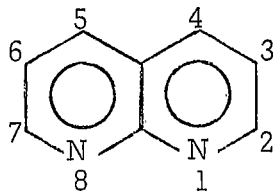
1,10-Phenanthroline

"phen"



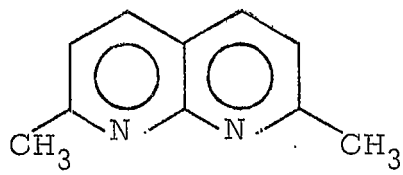
2,9-Dimethyl-1,10-phenanthroline

"dmp"



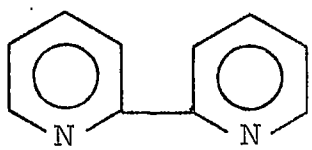
1,8-Naphthyridine

"NN"



2,7-Dimethyl-1,8-naphthyridine

"dmNN"



2,2'-Bipyridine

"bipy"

Heterocyclic molecules containing two nitrogen atoms.

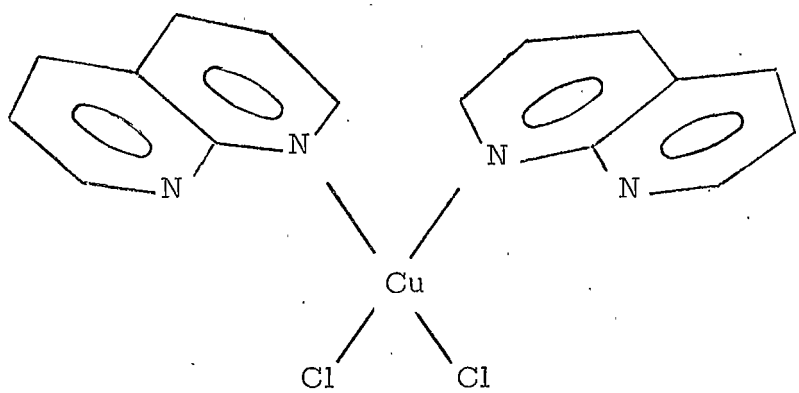
Figure 1

The compound 1,8-naphthyridine was prepared by Koller (15) and by Albert (16) by a multi-step sequence starting with methyl-2-aminonicotinate. Allen (17) reported the synthesis of 1,8-naphthyridine using 2-aminopyridine as the starting material. The synthesis of 2,7-dichloro-4-methyl-1,8-naphthyridine from 2,5-diaminopyridine was reported by Siede (18) in 1926. Ochiai and Miyaki (19) reported a catalytic hydrogenation scheme for conversion of 2,7-dichloro-4-methyl-1,8-naphthyridine to 4-methyl-1,8-naphthyridine. In 1964 the synthesis of 2-amino-7-hydroxy-1,8-naphthyridine from 2,6-diaminopyridine was reported (20). Enwall (21) synthesized 1,8-naphthyridine and its 4-methyl derivative by a four-step synthesis using 2,6-diaminopyridine.

All these previous syntheses which require a multi-step synthesis proceed in a low yield. Paudler and Kress (22, 23) reported in 1967 a one-step synthesis of 1,8-naphthyridine. They applied the Skraup reaction to 2-aminopyridine using meta-nitrobenzene sulfonic acid (sulfo-mix) as the oxidizing agent. The condensation of 2-aminopyridine employing sulfo-mix and glycerol gave 1,8-naphthyridine in 30% yield whereas the 2-amino-6-methylnaphthyridine reaction with crotonaldehyde and sulfo-mix produced 2,7-dimethyl-1,8-naphthyridine in 17% yield.

The first transition metal complex with 1,8-naphthyridine was synthesized and its structure determined by X-ray diffraction by Enwall (24) in this laboratory. Enwall (21) isolated $Cu(NN)_2Cl_2$ and

$Cu(NN)_2Br_2$. The former was a green crystalline substance and the latter an orange compound with a disordered crystal structure. Both compounds were crystallized out of aqueous solution and the chloride complex was shown to have a cis square planar structure. Naphthyridine is coordinated through one of its nitrogens; the uncoordinated nitrogens lie below and above the plane of the complex.



Bis(1,8-naphthyridine)copper(II)chloride

Figure 2

The copper-chloride distance is 2.25 Å, the copper-nitrogen distance is 2.02 Å, and the copper-uncoordinated nitrogen distance is 2.76 Å. The magnetic susceptibility measurement of the complex at room temperature showed that it had a normal magnetic moment of 1.90 B. M.

Hendricker and Reed (13) in 1969 reported the preparation and characterization of Group VIb metal carbonyl complexes with

2,7-dimethyl-1,8-naphthyridine. From the infrared spectra, carbonyl stretching frequencies, and their force constants compared with the five-membered ring nitrogen chelates they concluded that naphthyridine is a slightly better π-bonding ligand.

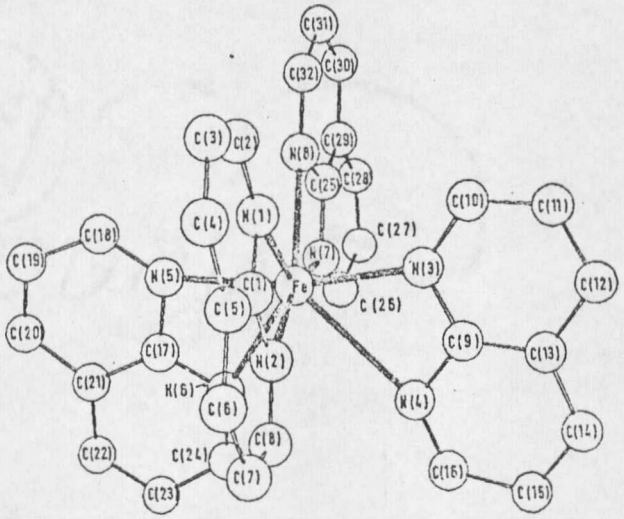
Hendricker (25) reported the dialkyltin dichloride adducts of this same ligand and from their infrared and pmr spectra he decided that the ligand forms a four-membered ring chelate with the central metal.

Hendricker and Bodner (26) isolated magnesium(II), calcium(II), strontium(II), and barium(II) perchlorate complexes of 1,8-naphthyridine and its 2,7-dimethyl derivative from anhydrous organic solutions. Complexes of 1,8-naphthyridine were hydrated, but complexes of 2,7-dimethyl-1,8-naphthyridine were anhydrous except for the magnesium(II) complex. The source of the water in hydrated compounds was not explained. From infrared and proton magnetic resonance spectra they concluded that all were chelated with naphthyridine through both nitrogens and the perchlorates were all coordinated to the central metal except in $Mg(dmNN)_2ClO_4)_2 \cdot 3.5\ H_2O$ where water molecules were coordinated to the metal instead of perchlorates.

These same authors (7,27) reported transition metal complexes of iron(II) to zinc(II) as well as cadmium, mercury, and silver with dmNN. Their anhydrous complexes had stoichiometry $M(dmNN)_3(ClO_4)_2$ except for mercury and silver, which were reported as bis (dmNN) complexes. From the infrared, ultraviolet, and visible spectra they assigned

octahedral geometry to all their tris compounds except $Cu(dmNN)_3^{2+}$. They did not observe any d-d transition for the copper(II) complex.

The above authors (1,2) also reported eight-coordinate transition metal complexes of NN with metal ions manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II), palladium(II), and cadmium(II). All complexes reported were anhydrous with stoichiometry $M(NN)_4(ClO_4)_2$. Their powder photograph data showed that complexes of manganese(II) to copper(II) were all isomorphic and that the cadmium and zinc compounds were similar. The structure of the $Fe(NN)_4(ClO_4)_2$ complex has been determined (3) by X-ray diffraction methods. The complex has a distorted dodecahedral geometry. The structure is shown in Figure 3.



Structure of tetrakis(1,8-naphthyridine)iron(II)perchlorate (3).

Figure 3

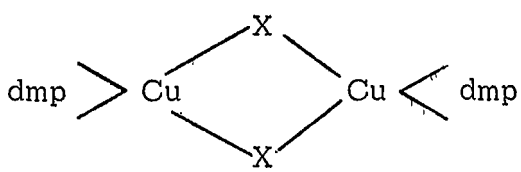
The iron-nitrogen distance varies from 2.18 to 2.75 Å. Four nitrogens, one from each naphthyridine molecule, are 2.18 to 2.25 Å distant from the iron atom; the other four nitrogens are all at significantly greater distances, 2.35 to 2.75 Å, indicating very unsymmetrical coordination of the naphthyridines. Coordination of the naphthyridine molecules through both nitrogens is in contrast to the monodentately coordinated ligand in $Cu(NN)_2Cl_2$ reported by Enwall (21). This raises a number of important and interesting questions about how the coordination should be described in these two types of complexes. These questions will require further study and have not been dealt with in this thesis.

NITROGEN COMPLEXES OF COPPER(I):— In the course of this investigation a number of copper(I) compounds were discovered which proved to have unusual properties; the literature on related compounds is summarized here.

Copper(I) complexes with various ligands, such as 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp), 2,2'-bipyridine (bipy), diazoaminobenzene, diazene and substituted diazenes have been studied (6,28,29). These complexes have been prepared either by reduction of copper(II) salts or by direct reaction of copper(I) salts and an appropriate base. Preparation and characterization of several copper(I) complexes of monosubstituted diazenes (RN=NH) have been reported (29). The crystal structures of $(CH_3N{=}NCH_3)Cu_2Cl_2$ and $(C_6H_5{-}N{=}N{-}N{-}C_6H_5)_2Cu_2$ have been

determined by X-ray diffraction methods (30,31). The $(CH_3N{=}NCH_3)Cu_2Cl_2$ molecule consists of infinite chains of copper and chlorine atoms with copper roughly tetrahedrally coordinated by three chlorine atoms in the chain and by a nitrogen lone pair from a diazene molecule (30). The $(C_6H_5\text{-}N{=}N\text{-}N\text{-}C_6H_5)_2Cu_2$ molecule exists in a dimeric form in which the diazoaminobenzene molecules are linked by nearly linear nitrogen-copper-nitrogen coordination to form an eight-membered ring with a copper-copper distance of 2.45 Å (31).

Reduction of 1,10-phenanthroline, or 2,2'-bipyridine complexes of copper(II) salts in ammoniacal solution with hydrazine, sodium bisulfite, or hydroxylamine has been reported by Tartarini (6). In some cases the copper(I) complexes were prepared directly from a mixture of copper(I) salt and the ligand. The preparation of $Cu(phen)_2I$, $Cu(bipy)I$, $Cu(phen)_2ClO_4$ and $Cu(bipy)_2ClO_4$ have been reported (6). These complexes were conductors in nitrobenzene solution and their spectrophotometric measurements showed the presence of the common ion CuL_2^+ (L = phen or bipy). There was also some evidence for a small amount of the bridged dimer of 2,9-dimethyl-1,10-phenanthroline (dmp) in equilibrium:



The following reaction has been proposed for the presence of ionic species in the solution of this complex:

$$2\,Cu(dmp)Cl \longrightarrow Cu(dmp)_2^+ + Cl^- + CuCl$$

The solution spectra showed absorption maxima at 21700 cm^{-1}, indicative of $Cu(dmp)_2^+$ ion (6). Petredis et al. (29) have also observed similar ionic species with copper(I) complexes in the solution and have isolated the $Cu(bipy)_2^+$ ion as its tetraphenylborate salt.

AIMS OF THIS RESEARCH:

All previous studies on transition metal complexes of 1,10-phenanthroline and 2,2'-bipyridine (Figure 1) have shown that these ligands coordinate through their two nitrogen atoms to the central metal. The $[Cu(phen)_2X]X$ and $[Cu(bipy)_2X]X$ compound (X= Cl or Br) were shown to contain five-coordinated copper(II) ion, where the metal has a trigonal pyramid geometry. When salts of anions other than halides were used, perchlorate and nitrate for instance, the ligands were still found to chelate in the same manner. By contrast, the report of the structure determination of $Cu(NN)_2Cl_2$ by X-ray diffraction methods showed that the naphthyridine molecule behaves differently (21). Both halogens are coordinated to the metal and the naphthyridines are coordinated through only one of the nitrogens. This was the only transition metal complex with 1,8-naphthyridine reported until 1968. This unexpected property of 1,8-naphthyridine compared with

1,10-phenanthroline and 2,2'-bipyridine stimulated interest in studies on transition metal complexes containing various anions. It has been pointed out (7) that in 1,8-naphthyridine and its 2,7-dimethyl derivative the electron pairs are extended in a parallel manner and separated by approximately 2.2 Å, whereas in phenanthroline the lone nitrogen pairs are not parallel but subtend an angle of about 85° at 2.00 Å from the metal center. This characteristic of the naphthyridine molecule, which is similar to that of carboxylate ion, results in the formation of polynuclear complexes with subnormal magnetic susceptibilities. Two such complexes have indeed been prepared during this work. Complexes of 2,7-dimethyl-1,8-naphthyridine were obtained to study the effect of the two methyl groups on coordination characteristics compared with the unsubstituted ligand. Isolation of metal perchlorate complexes with 1,8-naphthyridine from aqueous solutions was carried out to determine the effect of water of hydration on coordination characteristics of the ligand compared with anhydrous compounds reported in the literature (1,2,3). Complexes of metal salts of nitrate, sulfate, and acetate ions were also prepared to determine the effect of these anions on its coordinating powers. Finally, four copper(I) complexes of 1,8-naphthyridine and its 2,7-dimethyl-1,8-naphthyridine were isolated in order to investigate the nature of an incorrectly reported complex in the literature (7).

EXPERIMENTAL

ANALYTICAL TECHNIQUES

The ligand 1,8-naphthyridine and its 2,7-dimethyl derivative were prepared by using the Paudler and Kress procedures (21,22).

Reagent grade chemicals were used for all syntheses without further purification.

The copper(II) concentrations were determined by a titrimetric method using EDTA standard solution (0.01-0.02 M) and fast Sulphone Black F as end-point indicator (32). In some cases where the end-point was not sharp the iodometric method (33), using standard sodium thiosulfate solution (0.1 N), was applied.

Copper(I) concentrations were determined by iodometric titration (33) of an aqueous solution of the complex which had been previously air oxidized.

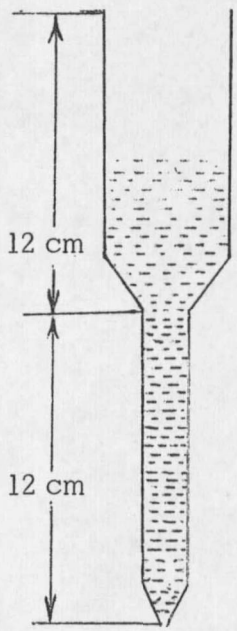
Manganese(II) and zinc(II) concentrations were estimated with standard EDTA solution using Eriochrome Black T as the end-point indicator (32).

Cobalt(II) concentrations were determined by EDTA titration which was previously used in this laboratory (34).

Nickel(II) was determined by gravimetric method using dimethylglyoxime as precipitant (32).

Silver(I) concentrations were determined by gravimetric procedure and precipitates were weighed out as silver(I) chloride (33).

Anion concentrations in the complexes were determined by an anion exchange method. A pyrex glass column which was made in this laboratory was used in this estimation. The shape and the measurements of this column are shown in Figure 4. The column was filled up to 15 cm with cation exchange resin, Dowex 50W-X8, and was regenerated with 6 M hydrochloric acid. In case of compounds containing silver, the column was regenerated with 6 M nitric acid. The column was washed with distilled water several times; about 15-25 mg of the sample was weighed exactly, then was dissolved in 10 ml of water or an organic solvent and was eluted through the column. After washing the



Schematic diagram of the ion-exchange column.

Figure 4

column with water three times, the eluted solutions were collected and titrated with standard 0.05 M sodium hydroxide to phenolphthalein end point. Figure 4 shows the schematic diagram of the column being used in this experiment.

Total carbon-hydrogen analyses were performed by Chemalytics Inc., Tempe, Arizona.

Conductance measurements were obtained in methanol or nitromethane solutions of the complexes using an Industrial Instruments Model RC-16B2 conductance bridge. The cell was calibrated with a standard potassium chloride solution prepared with conductance water.

The infrared spectra (4000-250 cm^{-1}) were obtained with a Beckman Infrared Spectrophotometer double-beam Model IR-20 in potassium bromide pellets. All spectra were calibrated with polystyrene film.

Diffuse reflectance spectra (360-800 nm) of the complexes were obtained with a Cary Model 1411 Diffuse Reflectance by using Type I illumination with integrating sphere attachment at Washington State University, Pullman, Washington.

All the electronic absorption spectra were measured in methanol or acetonitrile solutions of the compounds in matched 10-mm or 1-mm quartz cells using a Cary-14 recording spectrophotometer.

Magnetic susceptibilities were measured by the Gouy method using a Mettler analytical balance, Harvey-Wells L-44V electromagnet and a Magnion Model No. HS425 power supply. All susceptibilities

were determined at room temperature except those of $Cu(NN)Cl_2$ and $Cu(NN)Br_2$ which were determined at 196, 213.5, 250, 296, and 313°K. Four different field strengths were used in each study. The measurements at each field were run in triplicate and the average of the measurements was obtained. The data were used to calculate the gram susceptibilities from the equation:

$$\chi_g = \frac{2g.\Delta w}{d.A.H^2}$$

Where: g = acceleration of gravity

Δw = weight change

d = sample density

A = cross-sectional area of Gouy tube

H = magnetic field strength

Magnetic moments were obtained from the equation:

$$\mu_{eff.} = 2.84\,(\chi_M \cdot T)^{1/2}$$

Where: $\mu_{eff.}$ = magnetic moment expressed in Bohr magneton

χ_M = χ_g times sample molecular weight

T = degrees Kelvin.

The magnetic field was determined as described by Enwall (21). Diamagnetic corrections were calculated from the values given by Figgis and Lewis (35).

X-ray powder diffraction data were obtained using CuK_α radiation with the samples contained in 0.03-0.05 mm capillary glass tubes which

were mounted in a camera with a diameter of 57.3 mm on a Phillips Electronics Inc. power supply. X-ray single crystal data were collected by the Weissenberg method using CuK_{α} radiation.

PREPARATION OF COMPOUNDS

1. HALIDE COMPLEXES:

$Cu(NN)Cl_2$ and $Cu(NN)Br_2$:— A solution of 0.5 mmol of CuX_2 (X= Cl or Br) in 40 ml of 95% ethanol was heated to about 70°C and 0.05 mmol of NN was added. The solution was allowed to cool slowly until precipitation was completed. The olive-green $Cu(NN)Cl_2$ and the brown $Cu(NN)Br_2$ were collected by filtration, washed with a few milliliters of 95% ethanol, and air dried. The compounds were kept over calcium chloride overnight and were used without any further purification.

$Co(NN)_2Cl_2$:— To a solution of 0.238 g (1 mmol) of $CoCl_2 \cdot 6\,H_2O$ in 30 ml of absolute methanol 0.26 g (2 mmol) of NN in 10 ml of absolute methanol was added. This blue solution was kept in a closed chamber to avoid any possibility of water being absorbed from the atmosphere. The blue crystals which formed upon standing at room temperature were filtered, washed with absolute ethanol, and dried in a desiccator over calcium chloride. Further purification was performed from absolute methanol by the same procedure.

$Cu(dmNN)_2Cl_2$ and $Cu(dmNN)_2Br_2$:— Solutions of 1 mmol of $CuCl_2 \cdot 2\,H_2O$ or $CuBr_2$ in 30 ml of water were mixed with 0.316 g (2 mmol) of dmNN in 10 ml of absolute methanol. The gray-blue $Cu(dmNN)_2Cl_2$ precipitate and olive-green $Cu(dmNN)_2Br_2$ crystals were collected by filtration, washed with absolute methanol, and air dried. Both

compounds were recrystallized from absolute methanol and were finally dried over calcium chloride.

Table II

HALIDE COMPOUNDS

	% Calcd.				% Found				Color	Conductivity Λ(molar) cm^2 mho	Concn. $M \times 10^4$
	C	H	M[a]	A[b]	C	H	M	A			
$Cu(NN)Cl_2$	36.31	2.29	24.01	26.80	36.34	2.18	23.91	26.61	Olive-green	43[c]	15.19
$Cu(NN)Br_2$	27.18	1.71	17.97	45.21	27.78	1.68	17.84	45.18	Brown	67[e]	12.16
$Cu(NN)_2Cl_2$[d]	48.68	3.06	16.09	17.96	48.69	2.77	15.90	18.13	Green	51[e]	10.64
$Cu(NN)_2Br_2$[d]	39.73	2.50	13.14	33.04	39.78	2.63	13.36	33.42	Orange	58[c]	9.26
$Co(NN)_2Cl_2$			15.11	18.17			15.04	17.94	Blue	31[c]	11.80
$Cu(dmNN)_2Cl_2$	53.28	4.47	14.09	15.73	52.40	4.14	14.35	—	Blue	40[e]	8.56
$Cu(dmNN)_2Br_2$	44.50	3.73	11.77	29.61	44.19	3.57	11.66	—	Olive-green	64[e]	6.34
$Cu(py)_2Cl_2$	for comparison									50	18.6

[a] M = metal. [b] A = anion. [c] The conductivities were obtained in absolute methanol solutions.

[d] Were first synthesized by Enwall (21). [e] The conductivities were obtained in DMF solutions.

2. PERCHLORATE COMPLEXES:

$Cu(NN)_4(ClO_4)_2 \cdot 4H_2O$:— Aqueous solutions of 0.37 g (1 mmol) of cupric perchlorate hexahydrate and 0.52 g (4 mmol) of NN in 20 ml of water were mixed and the blue precipitate was collected in a sintered glass funnel. The blue substance was dried and then recrystallized from a mixture of acetone and absolute methanol (1:1). When this compound was recrystallized from water-acetone mixture (1:1) a blue hydrated crystalline compound was obtained. Upon leaving these crystals at room temperature for several minutes a blue powder was obtained. The analyses of this anhydrous compound along with hydrated crystals are given in Table III. Since the hydrated complex was not stable the carbon-hydrogen analysis was not possible. The weight loss in the compound which was determined by weighing the crystals before and after the decomposition was consistent with these determinations.

$Mn(NN)_4(ClO_4)_2 \cdot 4H_2O$, $Co(NN)_4(ClO_4)_2 \cdot 4H_2O$, $Ni(NN)_4(ClO_4)_2 \cdot 4H_2O$, and $Zn(NN)_4(ClO_4)_2$:— Solutions of 1 mmol of $M(ClO_4)_2 \cdot xH_2O$ (M = Mn, Co, Ni, and Zn) in 10 ml of water and 4 mmol of NN in 5 ml of water were mixed in a small Petri dish. The solutions were kept at room temperature partially covered until the crystallization was completed. The well-formed crystals were collected in a sintered glass funnel and air dried. The compounds were recrystallized from their aqueous solutions by similar procedure and were analyzed immediately after isolation. These hydrated compounds were not stable in

air, the loss of the water of hydration was observed gradually even at room temperature.

$Zn(NN)_2(ClO_4)_2 \cdot 4\,H_2O$:— To a solution of 0.264 g (1 mmol) of zinc(II) perchlorate hexahydrate in 5 ml of water 0.26 g (2 mmol) of NN was added and kept in a chamber containing absolute methanol. White lath-form crystals were obtained upon diffusion which were collected manually on a filter paper and dried over calcium chloride.

$Ag(NN)ClO_4$:— A solution of 0.13 g (1 mmol) of NN in 10 ml of warm water was added to a hot solution of 0.207 g (1 mmol) of silver(I) perchlorate in 50 ml of water. The solution was allowed to cool slowly until the crystallization was completed. The needle-form crystals were collected, washed with water followed by acetone, and dried over calcium chloride. The complex was recrystallized from hot water and dried as above.

Table III

PERCHLORATE COMPOUNDS

	% Calcd.				% Found				Color	Conductivity Λ(molar) cm^2 mho	Concn. M x 10^4
	C	H	M[a]	A[b]	C	H	M	A			
$Mn(NN)_4(ClO_4)_2 \cdot 4H_2O$			6.49	23.50			6.41	23.60	Yellow	197[c]	8.36
$Co(NN)_4(ClO_4)_2 \cdot 4H_2O$			6.23	23.38			6.29	23.15	Pink	207[d]	2.70
$Ni(NN)_4ClO_4)_2 \cdot 4H_2O$	45.20	3.79	6.90	23.39	44.66	3.55	6.78	23.28	Blue-green	181[d]	5.83
$Cu(NN)_4(ClO_4)_2 \cdot 4H_2O$			7.43	23.26			7.51	23.12	Blue	214[d]	3.23
$Zn(NN)_2(ClO_4)_2 \cdot 4H_2O$	32.21	3.38	10.96	33.34	32.12	3.05	11.18	33.72	White	208[c]	7.14
$Co(NN)_4(ClO_4)_2$[e]	49.38	3.11	7.57	25.55	49.37	2.92	7.53	25.79	Pink	198[c]	8.92
$Cu(NN)_4(ClO_4)_2$[e]	49.08	3.09	8.11	25.40	48.79	2.82	8.18	25.60	Blue	206[c]	5.13
$Zn(NN)_4(ClO_4)_2$[e]			8.33	25.34			8.30	25.27	White	203[c]	4.28
$Ag(NN)ClO_4$			31.96	29.47			31.75	29.51	White	102[d]	2.14

[a] M = metal. [b] A = anion. [c] The conductivities were obtained in nitromethane solutions. [d] The conductivities were obtained in absolute methanol solutions. [e] Previously reported (1).

3, NITRATE COMPLEXES:

$Co(NN)_4(NO_3)_2 \cdot 6H_2O$, $Ni(NN)_2(NO_3)_2 \cdot 4H_2O$, and $Zn(NN)_4(NO_3)_2 \cdot 6H_2O$:— Solutions of 1 mmol of $M(NO_3)_2 \cdot 6H_2O$ (M = Co, Ni, or Zn) in 10 ml of water and 0.521 g (4 mmol) of NN in 5 ml of water were mixed and kept in a partially open Petri dish at room temperature until the crystallization was completed. The crystals were collected, washed with 95% ethanol and dried over calcium chloride in a desiccator. The compounds were recrystallized from their aqueous solutions by a similar procedure. These compounds were not stable at room temperature, the water of hydration being lost upon standing in air or over calcium chloride.

$Mn(NN)_2(NO_3)_2$:— Commercially available 50% manganese nitrate solution, 5 ml, was mixed with 0.26 g (2 mmol) of NN in a Petri dish and was kept covered in a dark place for about one week. The yellow well-formed crystals were separated manually on a filter paper and were washed with chloroform. The crystals were kept in a closed vial covered with black paper to protect the crystals from decomposition, and kept in a desiccator. This compound was hygroscopic and light sensitive. When solution of the compound was exposed to the light a black precipitate, not very soluble in inorganic acids, was obtained. No identification of this black substance was made.

$Cu(NN)_{2.16}(NO_3)_2$ and $Cu(NN)_2(NO_3)_2$:— Solutions of 0.296 g (1 mmol) of cupric nitrate hexahydrate in 10 ml of water and 0.39 g

(3 mmol) of NN in 5 ml of water were mixed and kept in a partially covered Petri dish. Upon slow evaporation of the solution at room temperature, blue crystals were isolated after a few days. The crystals were collected by filtration, washed with a small volume of chloroform, and air dried. Further recrystallization of the compound from its aqueous solution was carried out by the same method. The compound was dried over calcium chloride and analyzed as $Cu(NNO_{2.16}(NO_3)_2$. When 0.2 g of this complex was dissolved in 30 ml of absolute methanol containing 10 ml of 2,2'-dimethoxypropane and was refluxed for 8 hours a blue substance was obtained. This compound was collected by filtration, washed with chloroform, and dried over calcium chloride. The stoichiometry of the complex was proved by its elemental analyses as $Cu(NN)_2(NO_3)_2$. This latter bis complex was also prepared by dissolving an appropriate ratio of the cupric nitrate and NN in dry methanol by a similar method.

$Co(NN)_2(NO_3)_2$:— A solution of 0.291 g (1 mmol) of cobalt(II) nitrate hexahydrate in 10 ml of absolute ethanol was mixed with 0.26 g (2 mmol) of NN in a 25-ml beaker. This solution was kept in a closed chamber for a few days until the pink crystals were isolated. The crystals were collected manually on a filter paper and dried over calcium chloride. This anhydrous substance was not stable and it absorbed water from the atmosphere upon standing in air. The reproducibility of this bis compound was poor and most of the time it was isolated with

different numbers of hydration water. The hydration number varied with the solvent impurity as well as the period of time it was kept in solution during the crystallization.

$Ag(NN)NO_3$:— A solution of 0.17 g (1 mmol) of $AgNO_3$ in 50 ml of water was mixed with 0.13 g (1 mmol) of NN in 10 ml of water. The white precipitate was collected by filtration, washed with acetone, and air dried. This white substance was dissolved in a sufficient amount of hot water and allowed to cool slowly. The white needles were collected on a sintered glass funnel and washed with a few milliliters of 95% ethanol. The crystals were air dried and kept in a desiccator over calcium chloride.

Table IV

NITRATE COMPOUNDS

	% Calcd.				% Found				Color	Conductivity[c] ∧(molar) cm^2 mho	Concn. $M \times 10^4$
	C	N	M[a]	A[b]	C	H	M	A			
$Mn(NN)_2(NO_3)_2$			12.51	28.23			12.77	28.09	Yellow	182	6.33
$Co(NN)_2(NO_3)_2$			13.30	27.98			13.08	27.81	Pink	187	14.32
$Cu(NN)_2NO_3)_2$	42.91	2.70	14.19	27.68	42.99	2.62	14.34	27.99	Blue	152	13.17
$Cu(NN)_{2.16}(NO_3)_2$	44.35	2.79	13.53	26.40	43.96	2.76	13.64	26.52	Blue	136	12.22
$Ni(NN)_2(NO_3)_2 \cdot 4H_2O$	37.31	3.91	11.40	24.08	37.64	3.56	11.31	23.92	Blue-green	185	8.97
$Co(NN)_4(NO_3)_2 \cdot 6H_2O$	47.35	4.47	7.26	15.28	47.34	4.43	7.58	15.57	Pink	208	7.14
$Zn(NN)_4(NO_3)_2 \cdot 6H_2O$	46.98	4.44	7.99	15.16	47.33	4.25	8.22	15.39	White	174	11.56
$Ag(NN)NO_3$			35.95	20.67			35.72	20.88	White	90	21.73

[a] M = metal. [b] A = anion. [c] All the conductivities were obtained in absolute methanol solutions.

4. COPPER(I) COMPLEXES:

$Cu_2(NN)Cl_2$ and $Cu_2(dmNN)Cl_2$:— To a solution of 0.198 g (1 mmol) of CuCl in 40 ml of warm acetonitrile 0.065 g (0.5 mmol) of NN or 0.079 g (0.5 mmol) of dmNN in 10 ml of acetonitrile was added. The orange precipitate was collected by filtration, washed with absolute methanol, and air dried. These compounds were not soluble in most ordinary organic solvents. Aqueous solutions of these compounds were unstable in air and the copper(I) was air oxidized to a green copper(II) species. The preparation of these complexes under nitrogen atmosphere gave pure products which were used without any further purification.

$Cu(NN)ClO_4$:— To a solution of 0.1 g of $Cu(NN)_4(ClO_4)_2$, in 30 ml of absolute methanol, 10 ml of 2,2'-dimethoxypropane was added. This solution was refluxed for four hours and 0.3 g of cupric perchlorate hexahydrate was added. After refluxing this solution for 12 hours it was concentrated with warming under reduced pressure to one-half the volume and kept under nitrogen in a chamber containing a beaker of sodium hydroxide pellets. The orange crystals were collected by filtration, washed with chloroform, and dried over calcium chloride. The compound was recrystallized from nitromethane solution by a similar method.

$Cu(dmNN)_2ClO_4$:— A solution of 0.14 g (0.42 mmol) of cupric perchlorate hexahydrate in 40 ml of absolute methanol and 10 ml of 2,2'-dimethoxypropane was refluxed for six hours followed by the addition of 0.158 g (1 mmol) of dmNN. After refluxing for 18 hours the light brown

solution was allowed to cool slowly. The brown needles were collected by filtration and were recrystallized from absolute methanol or nitromethane. The product was washed with chloroform and dried over calcium chloride.

Table V

COPPER(I) COMPOUNDS

	% Calcd.				% Found				Color	Conductivity Λ(molar) cm^2 mho	Concn. M x 10^4
	C	H	M[a]	A[b]	C	H	M	A			
$Cu_2(NN)Cl_2$	29.28	1.85	38.73		29.36	1.62	38.83		Orange	132[c]	9.81
$Cu_2(dmNN)Cl_2$	33.72	2.83	35.68		34.45	2.85	35.39		Orange	122[c]	9.09
$Cu(NN)ClO_4$	32.78	2.06	21.67		32.67	2.00	21.36		Orange	101[d]	15.62
$Cu(dmNN)_2ClO_4$	50.10	4.20	13.25	20.74	50.20	4.25	12.98	20.69	Brown	112[e]	0.84

[a] M = metal. [b] A = anion. [c,d,e] The conductivities were obtained in: acetonitrile (c), nitromethan (d), and absolute methanol (e) solutions.

RESULTS AND DISCUSSION

PART I — HALIDE COMPLEXES:

The analytical and physical data for halide complexes are reported in Table II. Attempts to determine the melting point of the complexes were unsuccessful due to decomposition of the compounds at temperatures of about 240°C. The compounds are all stable on exposure to light and air except $Cu(dmNN)_2Cl_2$, which gradually changes from blue to brown upon standing in sunlight for two weeks.

The magnetic susceptibilities of all copper(II) complexes were determined and from the observed susceptibilities the magnetic moments per copper atom were evaluated. The magnetic moments of all complexes (Table VI), apart from mono-complexes, lie in the range 1.99-2.01 B.M. The normal magnetic moment associated with copper(II) compounds is 1.8-2.2 B.M. (12). From this it is concluded that the copper(II) complexes of NN and dmNN with magnetic moments of 1.99-2.01 B.M. are mononuclear; on the other hand, the $Cu(NN)Cl_2$ and $Cu(NN)Br_2$ complexes with room temperature magnetic moments of 1.69 B.M. and 1.59 B.M. respectively are similar to those of copper(II) carboxylates (12). As noted in the introduction, these latter compounds exhibit subnormal magnetic moments, and have a maximum in a plot of molar magnetic susceptibility versus temperature. The magnetic susceptibilities of the $Cu(NN)Cl_2$ and $Cu(NN)Br_2$ compounds were determined at several different temperatures and it was found that they were

Table VI

MAGNETIC SUSCEPTIBILITY OF DATA OF HALIDE COMPLEXES

Compound	Diamagnetic Correction c.g.s.u. $\times 10^6$	Corr. $\chi_M \times 10^6$ c.g.s.u.	T, ^oK	$\mu_{eff.}$ B.M.
$Cu(NN)_2Cl_2$	193	1704	296	2.01
$Cu(NN)_2Br_2$	217	1670	296	1.99
$Co(NN)_2Cl_2$	193	8149	298	4.40
$Cu(dmNN)_2Br_2$	263	1670	296	1.99
$Cu(NN)Cl_2$	120	1107	326	1.70
		1153	313	1.70
		1201	297	1.69
		1376	250	1.66
		1497	213.5	1.60
		1530	196	1.55
$Cu(NN)Br_2$	143	1081	326	1.68
		1035	313	1.61
		1066	296	1.59
		1109	250	1.49
		1163	312.5	1.41
		1110	196	1.32

temperature dependent and similar to copper(II) acetate monohydrate (Table VI). In Figure 5, plots of molar magnetic susceptibilities versus temperature are shown. The $Cu(NN)Br_2$ has a maximum at about 215°K and the maximum for $Cu(NN)Cl_2$ is below 196°K. The $Cu_2(CH_3COO)_4 \cdot 2\,H_2O$ curve is shown for comparison, with maximum at about 260°K. These data suggest that these two complexes are bridged binuclear molecules.

Since halide bridged copper(II) compounds are very common, and this subnormal magnetic behavior was observed only in halide complexes it is possible that these might be halide bridged dimers. It has been reported in the literature that copper(II) compounds containing halide bridges do not exhibit subnormal magnetic properties at room temperature (36). Thus it seems likely that 1,8-naphthyridine molecules are bridged across the two copper atoms in $Cu(NN)Cl_2$ and $Cu(NN)Br_2$ compounds.

Molecular weights would be useful on confirming the above hypothesis but the sparing solubilities of the copper(II) halide compounds prevented the determination of molecular weights.

By comparison of X-ray powder photographs, it was found that the crystals of $Cu(NN)Cl_2$ and $Cu(NN)Br_2$ were isomorphous which will be discussed in the following paragraphs.

The comparison of $Cu(NN)Cl_2$ and $Cu(NN)Br_2$ infrared spectra showed that both were similar in the region 4000-300 cm^{-1}. The ligand

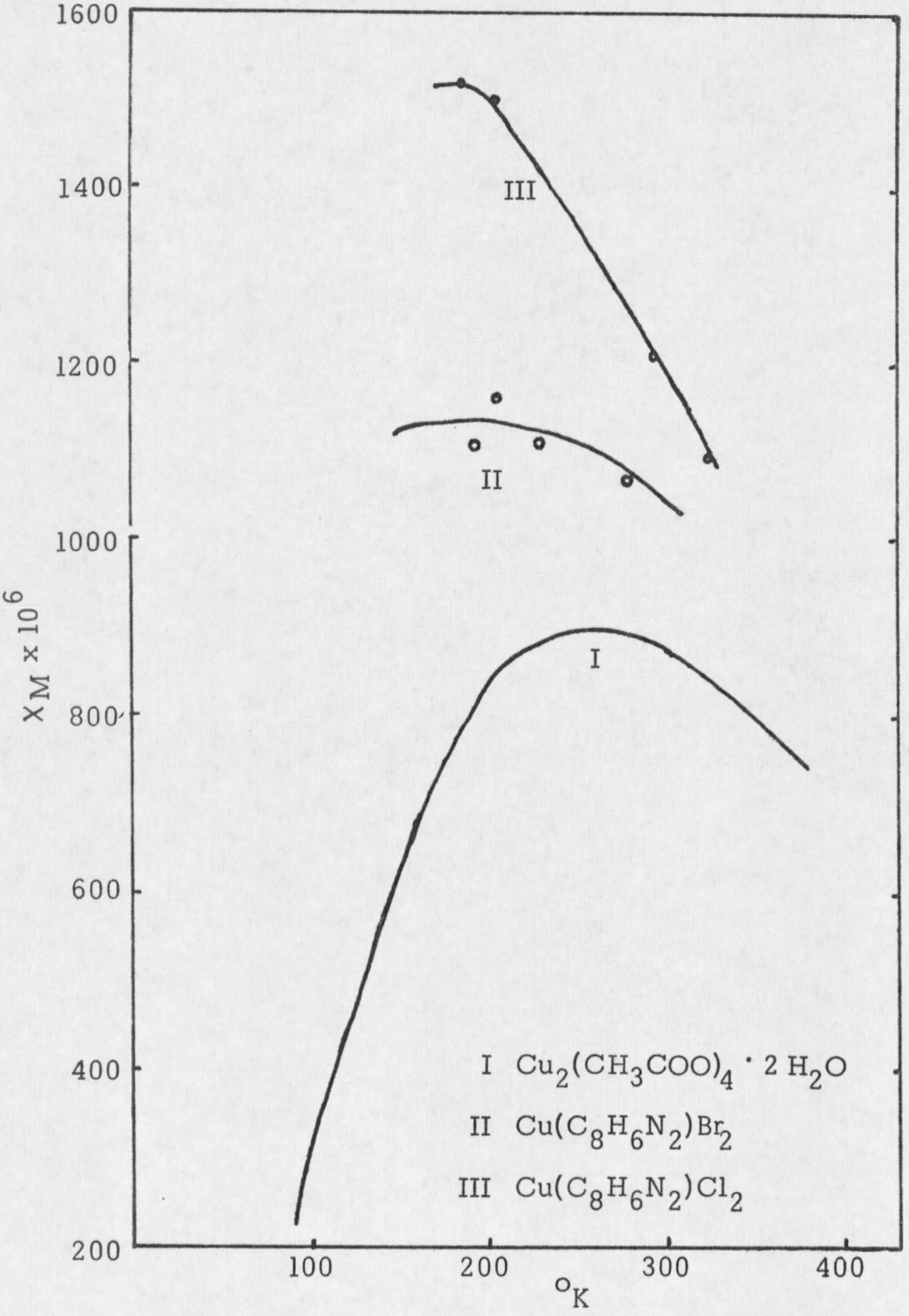
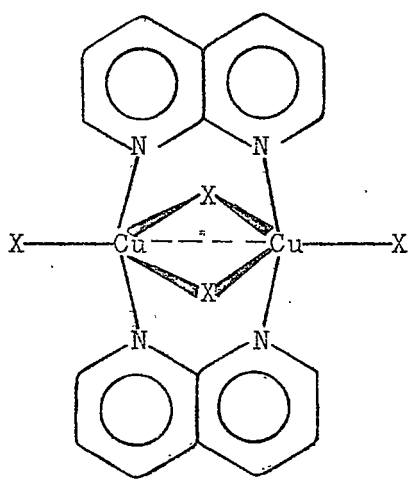
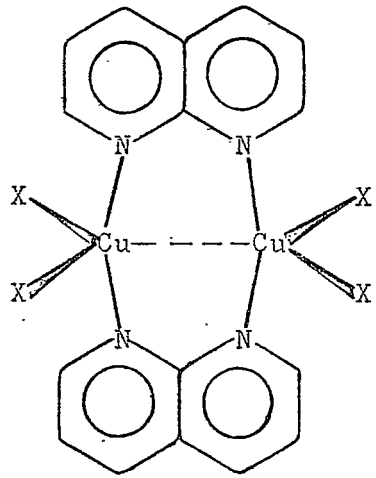


Figure 5. Magnetic susceptibilities of the subnormal Copper(II) complexes.



A



B

POSSIBLE STRUCTURES FOR $Cu(NN)Cl_2$ AND $Cu(NN)Br_2$.

Figure 6.

mode for 1,8-naphthyridine have been assigned and recorded in the range 1700-650 cm^{-1} by Armarego et al. (37). As would be expected, the ligand infrared spectrum altered on coordination. In Table VII, the ligand modes which shift significantly upon coordination and the parent ligand vibrations are listed.

Previous studies (38) on complexes containing metal-halogen bonds indicate that the metal-chlorine stretching frequencies occur between 350-250 cm^{-1} and metal-bromine frequencies from below 250-200 cm^{-1}. The bridged copper-chlorine and terminal copper-chlorine stretching vibrations have been observed at 311 cm^{-1} and 326-330 cm^{-1} respectively (39,40). The terminal copper-chlorine stretching vibrations in $Cu(py)_2Cl_2$ and $Et_4N)_2CuCl_4$ compounds have been reported at 287 cm^{-1} and 268-289 cm^{-1} respectively (41,42). In Table VIII, the copper-chlorine stretching frequencies for bridged and terminal chloride ions, in some copper(II) complexes are listed. The terminal copper-chlorine stretching frequency in $Cu(NN)_2Cl_2$ complex (see Figure 8) occurs as a single broad band with the absorption maximum at 282 cm^{-1} which is in good agreement with the values reported for $Cu(py)_2Cl_2$ and $(Et_4N)_2CuCl_4$ compounds. In $Cu(NN)Cl_2$ the shape of this band is quite different and shifts to higher frequency (see Figure 8) which indicates different copper-chlorine bond(s) compared with the $Cu(NN)_2Cl_2$ complex containing two terminal chloride ions (Figure 2). The copper-bromine stretching frequencies were not observed in this study which

Table VII

SELECTED INFRARED ABSORPTIONS (400-250 CM^{-1}) OF HALIDE COMPLEXES*

Band	NN	$Cu(NN)Cl_2$	$Cu(NN)Br_2$	$Cu(NN)_2Cl_2$	$Cu(NN)_2Br_2$	$Co(NN)_2Cl_2$
I	1555 vs	1572 s	1570 m	1580 s	1570 s	1565 s
II	1492 vs	1510 vs	1510 vs	1495 vs	1502 vs	1502 vs
III	1360 w,sh	1350 s	1350 s	....	....	....
IV	1288 s	1240 m	1240 w	1236 vs	1240 m	1234 m
V	....	....	....	....	1147 m	1145 s
VI	1128 vs	1138 s	1138 m	1136 s	1128 s	1128 s
VII	1045 m	1082 m	1082 w	1057 m	1062 s	1063 s
VIII	1026 s	1055 vw	1056 vw	1031 m	1035 m	1035 m
IX	969 vs	982 m	981 w	968 vw	970 vw	970 vw
X	953 vw	965 w	963 vw	958 vw	960 vw	957 w
XI	835 vs	848 vw	847 s	842 s,sh	845 s,sh	840 vs
XII	809 vs	842 s	842 s	835 vs	840 vs	835 s,sh
XIII	773 m,sh	830 m	834 m,sh	800 vs	800 vs	803 vs
XIV	760 vs	790 vs	790 vs	780 vs	785 vs	785 vs
XV	600 w	640 vw	638 vw	622 m	630 w	627 m
XVI	402 m	437 m	435 vw	420 m	427 w	426 m
XVII	300 vw	300 s,br	300 vw	282 vs,br	275 w,sh	310 s
XVIII	272 vw	290 m	280 vw,sh	....	265 w,sh	285 m
XIX	....	245 s	245 s	....	....	257 m

* The assignments are: s, strong; v, very; m, medium; sh, shoulder; br, broad; w, weak.

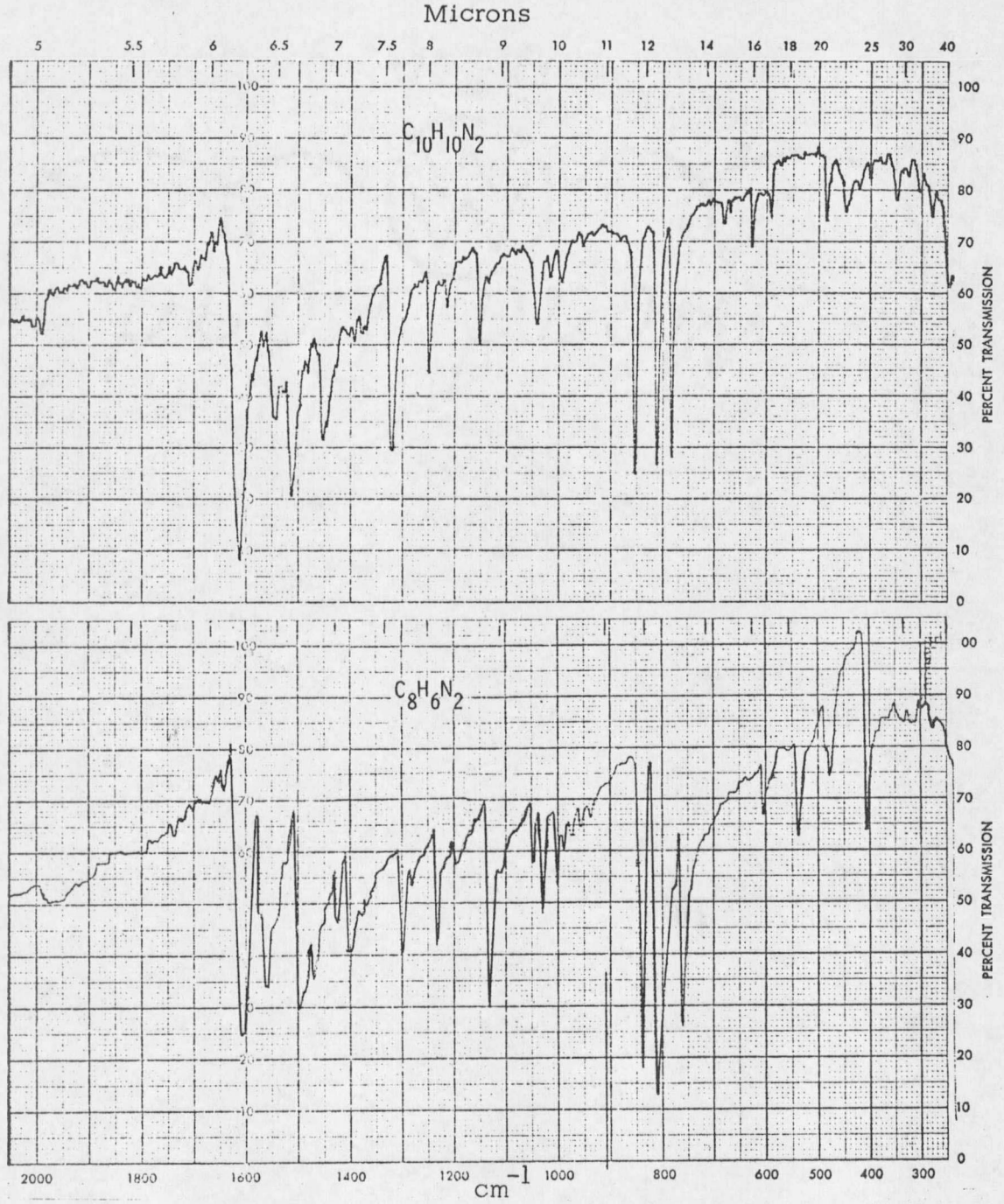


Figure 7. Infrared Spectra of $C_{10}H_{10}N_2$ and $C_8H_6N_2$.

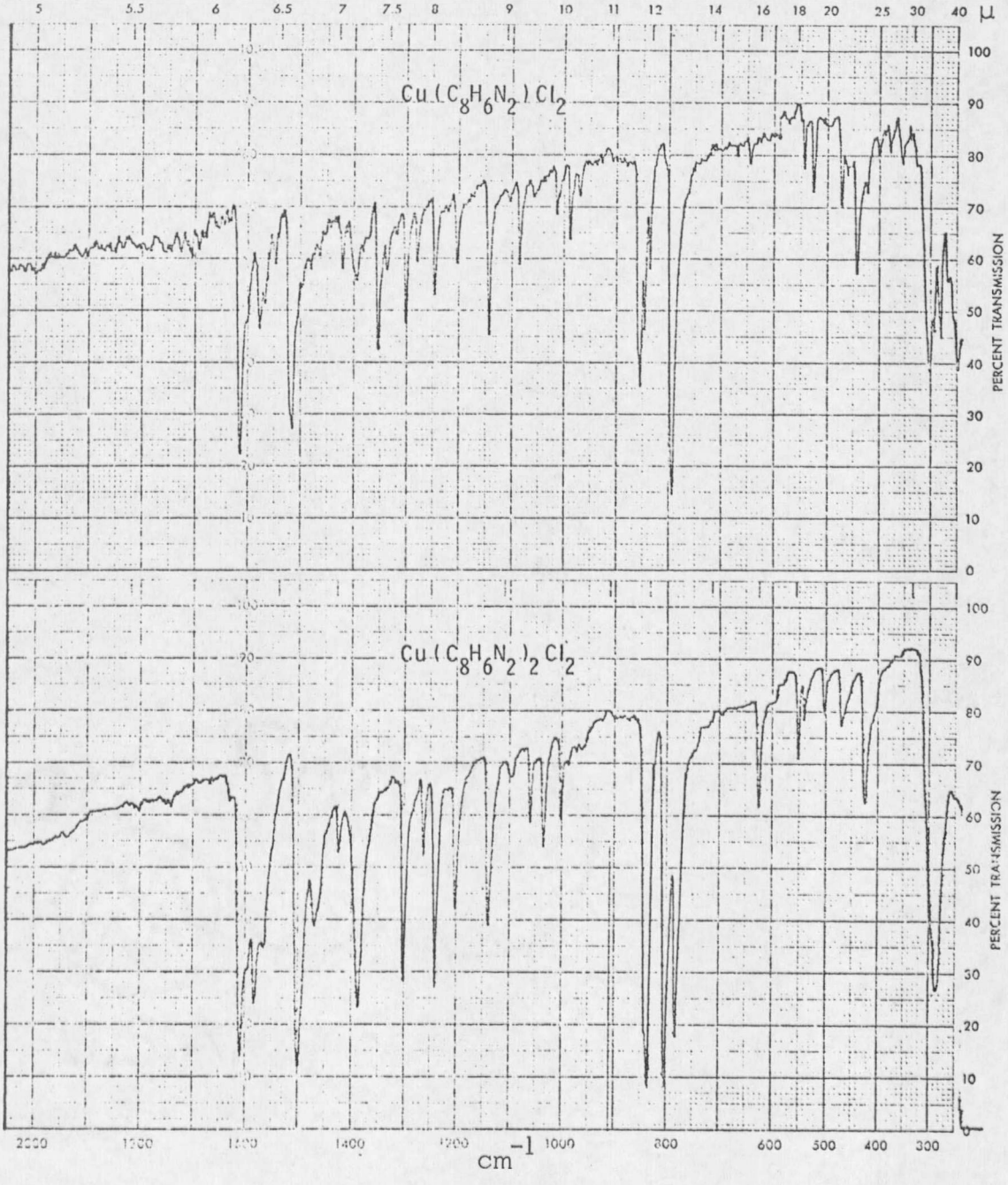


Figure 8. Infrared Spectra of $Cu(C_8H_6N_2)Cl_2$ and $Cu(C_8H_6N_2)_2Cl_2$.

Table VIII

INFRARED ABSORPTIONS OF SOME Cu(II) COMPLEXES [a]

	μ, B.M.	Cu-Cl[b], CM^{-1}
$Cu(NN)_2Cl_2$	2.01	282
$Cu(NN)Cl_2$	1.69	300, 290
$[(PyO)CuCl_2]_2$[c]	0.59-1.06, 0.63	330, 311
$[(3\text{-}CH_3PyO)CuCl_2]_2$	0.55, 0.97	320
$[(4\text{-}CH_3PyO)CuCl_2]_2$	0.49, 0.52	327, 312
$[(PyO)_2CuCl_2]_2$	0.46, 0.63	310, 280
$(2\text{-}CH_3PyO)_2CuCl_2$	1.95	328
$(3\text{-}CH_3PyO)_2CuCl_2$	....	322
$[2,6\text{-}(CH_3)_2PyO]_2CuCl_2$	1.91	319, 297
$Cu_3Cl_6[4\text{-}Cl(quinO)]_2$[c]	2.07	308, 290
$CuCl_2(4\text{-}Cl\text{-}Py)_2$[c]	1.83	294[d]
$CuCl_2(Py)_2$	....	287
$(Et_4N)_2CuCl_4$[e]	....	289 sh, 268

[a] Reference 39. [b] Commas separate more than one infrared band.

[c] PyO = pyridine N-oxide; QuinO = quinoline N-oxide; Py = pyridine.

[d] Reference 42. [e] Reference 42.

indicates that the bands observed at 300(s,br) cm^{-1} and 290(m) cm^{-1} are copper-chlorine stretching vibrations of $Cu(NN)Cl_2$ complex.

The reflectance spectra of copper(II) halide complexes of 1,8-naphthyridine are shown in Figure 9 and their absorption maxima are listed in Table IX. The diffuse reflectance spectra of $Cu(NN)Cl_2$ and $Cu(NN)Br_2$ are similar with absorption maxima at 13240 cm^{-1} and 13160 cm^{-1} respectively which is consistent with the weaker ligand field strength of bromide compared with chloride.

From magnetic susceptibility measurements, X-ray powder photographs, and visible and unfrared spectra of $Cu(NN)X_2$ (X= Cl or Br) there are several possible structures which can be suggested for these complexes. Among all possible structures there is only one structure which fits the data. In Figure 6-A, a dimer molecule of $Cu(NN)X_2$ is shown in which two naphthyridine molecules are coordinated through two nitrogens across the two Cu(II) ions with two halogen atoms forming bridges in the plane perpendicular to the plane of the naphthyridine molecules and two terminal halogens on each side of the binuclear complex. These two terminal halogens may coordinate to the neighboring molecules unsymmetrically, giving rise to one short and one long copper-chlorine bond distance. Figure 6-B shows an alternative possible structure in which copper atoms are bridged in pairs by two naphthyridine molecules with the four halide ions occupying terminal positions. In Figure 6-B, both terminal chloride ions are equivalent

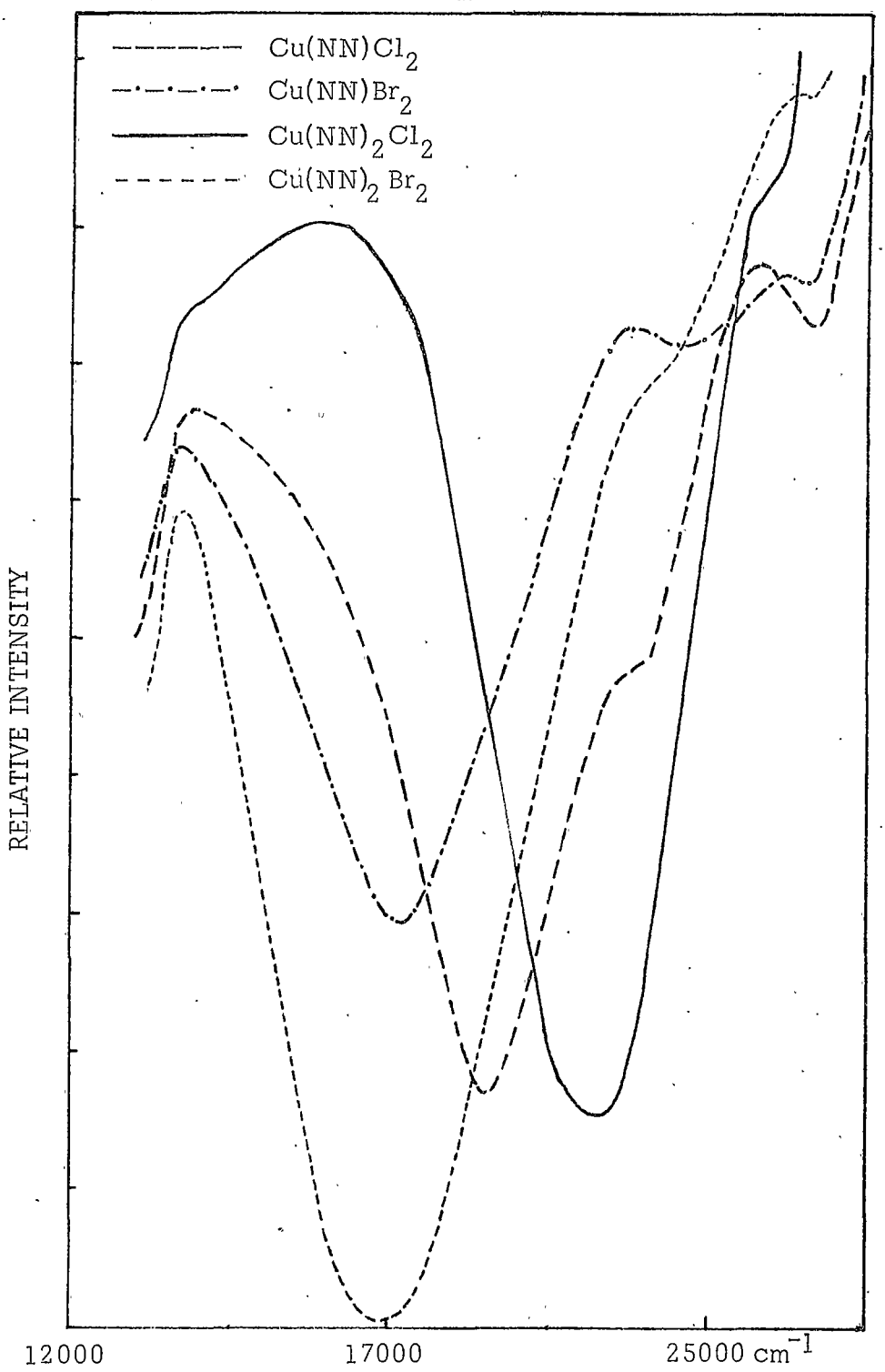


Figure 9. Diffuse reflectance of halide complexes.

Table IX

VISIBLE ABSORPTION SPECTRA OF HALIDE COMPLEXES (CM^{-1})

	Charge-transfer and ligand bands	d-d bands
$Cu(NN)Cl_2$	26800, 21980 sh	14660 sh, 13240
$Cu(NN)Br_2$	28400, 21740	14490 sh, 13160
$Cu(NN)_2Cl_2$	27030 sh	14800, 13330 sh
$Cu(NN)_2Br_2$	28170 sh, 22470 sh	13000
$Co(NN)_2Cl_2$*		17180, 16750, 16390, 15950

* The spectrum was obtained in nitromethane solution.

and the copper-chlorine stretching vibrations would appear as a single band, as is observed in the $Cu(NN)_2Cl_2$ spectrum. The infrared vibration frequencies of copper-chlorine stretching bands in $Cu(NN)Cl_2$ complex indicate that the chloride ions are not equivalent and they probably have different types of coordination to the copper(II) ion. This is in agreement with the structure 6-A which contains two different kinds of chlorines coordinated to the copper atom. The structure 6-B contains only one kind of copper-halogen bond, whereas the infrared spectrum seems to call for two.

$Cu(NN)_2Cl_2$ and $Cu(NN)_2Br_2$:— The magnetic moments of these complexes (Table VI) indicate that the molecules exist as mononuclear

species. The X-ray powder photographs showed differences indicating that these complexes are not isomorphic. The infrared spectrum of $Cu(NN)_2Br_2$ was compared with those of $Cu(NN)_2Cl_2$, $Cu(NN)Cl_2$, and tetrakis nitrate and perchlorate complexes which contain bidentately coordinated naphthyridine in the region 4000-300 cm^{-1}. The ligand modes of the bis halide complexes are listed in Table VII. The band at 1350 cm^{-1} which occurs in $Cu(NN)Cl_2$ is not present in the $Cu(NN)_2Br_2$ spectrum and a new band at 1147 cm^{-1} has appeared. The splitting of the ligand band at 1128 cm^{-1} into two bands at 1128 cm^{-1} and 1145 cm^{-1} has also been reported (26) for dmNN complexes in which 2,7-dimethyl-1,8-naphthyridines were coordinated through both nitrogens to the metal ions. The infrared spectrum of the $Cu(NN)_2Br_2$ complex was similar to the spectra of the tetrakis perchlorate complexes (see Figure 3) in which naphthyridines were coordinated through both nitrogens to the metal ion. The splitting of the ligand band at 1128 cm^{-1} was not observed in perchlorate complexes because this region of the spectra was covered by very strong and broad band of perchlorate anion. The spectra of perchlorate complexes were superimposable, apart from perchlorate and nitrate bands, on spectra of nitrate complexes in which the splitting of the 1128 cm^{-1} ligand bands was observed (see Table XVIII). The agreement of the $Cu(NN)_2Br_2$ infrared spectrum with those of chelated complexes suggests that the naphthyridine molecules are coordinated through both nitrogen atoms to the metal ion. The

copper-bromine stretching frequencies were not observed in this study since they were beyond the range of the instrument available to us. This also indicates that the band observed at 282(vs,br) cm^{-1} in $Cu(NN)_2Cl_2$ is copper-chlorine stretching vibration since it was not observed in $Cu(NN)_2Br_2$ complex.

The reflectance spectra of $Cu(NN)_2Cl_2$ and $Cu(NN)_2Br_2$ in the visible region are shown in Figure 9 and the absorption bands are listed in Table IX. The $Cu(NN)_2Cl_2$ spectrum contains a broad band with an ill-defined maximum in the region 15000-13000 cm^{-1} whereas the spectrum of $Cu(NN)_2Br_2$ showed comparatively sharp band with absorption maximum at 13000 cm^{-1} which again indicates that the geometries of the two complexes are not similar. Above 2000 cm^{-1} the absorption rises sharply due to charge transfer and ligand bands (see Figure 9 and Table IX). Several copper(II) compounds with different geometries and visible absorption band(s) are listed for comparison in Table X. The position of the absorption bands in copper(II) complexes varies greatly with different coordination geometries. To assign a geometry to the $Cu(NN)_2Br_2$ from its visible absorption band is clearly not possible, but the spectrum is similar to those of distorted octahedral complexes. The molar conductivity of the $Cu(NN)_2Br_2$ in absolute methanol solution (Table II) indicated that the complex was not ionic and the infrared spectrum suggested coordination of the ligands through both nitrogens. Thus a

Table X

ELECTRONIC ABSORPTION SPECTRA OF SOME Cu(II) HALIDES[a]

Compound	Geometry	Visible Bands, cm^{-1}	
$Cu(Dmq)Cl_2$[b]	dist. oct.	18690 sh	14180
$Cu(Dmq)Br_2$	dist. oct.		14925
Trans-$Cu(Dpq)_2Cl_2$[b]	squ. planar	18690	14290
Trans-$Cu(Dpq)_2Br_2$	squ. planar		14925
$Cu(Mq)_2Cl_2$[b]	dist. oct.		14700
$Cu(Mq)_2Br_2$	dist. oct.		16130
$Cu(bipy)_2Cl_2$[c]	tetragonal	28000	12800
$Cu(bipy)_2Br_2$[c]	pyramidal	26700	12800
$CuCl_2 \cdot 2NH_3$[d]	dist. oct.		14850
$CuBr_2 \cdot 2NH_3$[d]	dist. oct.		14800
$CuCl_2py_2$[e]	dist. oct.		14500
Cu(4-MeT)Cl_2[f]	dist. oct.	25600	13300

[a] Reference 44. [b] Dmq = 2,3-dimethylquinoxaline; Dpq = 2,3-diphenylquinoxaline; Mq = 2-methylquinoxaline. [c] Reference 45. [d] Reference 46. [e] References 43, 47. [f] 4-Met = 4-methylthiazole; reference 48.

distorted octahedral geometry for the copper(II) ion surrounded by four nitrogens and two bromine atoms seems likely.

$Cu(dmNN)_2Cl_2$ and $Cu(dmNN)_2Br_2$:— The infrared spectra of the olive-green $Cu(dmNN)_2Br_2$ and the blue $Cu(dmNN)_2Cl_2$ were identical and also were superimposable on the spectrum of the brown $Cu(dmNN)_2Cl_2$ which was obtained from decomposition of the blue derivative upon exposure to sunlight for two weeks. The ligand modes which shift significantly upon coordination and the free ligand vibrations are listed in Table XI. The assignment of the ligand modes has been reported in the literature (7). In the spectra of these complexes the ligand band at 1128 cm^{-1} was not observed after coordination and only one strong band at 1147 cm^{-1} was present. This appearance of a single band in the region 1100-1200 cm^{-1} is similar to the single band observed at 1136(s) cm^{-1} in $Cu(NN)_2Cl_2$ in which naphthyridines were coordinated through one of the nitrogens to the copper ion. This is in contrast to the infrared spectra of the dmNN complexes reported in the literature (26) in which naphthyridines were chelated and showed two bands at 1128 cm^{-1} and 1145 cm^{-1}. The infrared absorption bands were compared with that of the iron complex, $Fe(dmNN)_3(ClO_4)_2$ (7). The ligand bands at 847(vs), 805(vs), and 778(vs) cm^{-1}, which are sensitive to coordination and shift to 870(s), 853(s), and 803(vs) cm^{-1} respectively in iron(II) complex, were observed as five bands at 868(vs), 815(m, sh), 810(s), 803(vs), and 777(w) cm^{-1} (Table XI) in $Cu(dmNN)_2^{2+}$ halide

Table XI

SELECTED INFRARED ABSORPTIONS (4000-250 CM^{-1}) OF $Cu(dmNN)_2X_2$*

Band	dmNN	$Cu(dmNN)_2Cl_2$	$Cu(dmNN)_2Br_2$
I	1532 m	1570 s	1567 s
II	1360 w	1380 s	1380 s
III	1240 s	1255 s	1253 s
IV	1205 m	1220 m	1220 m
V	847 vs	868 vs	867 vs
VI	....	815 m, sh	816 m, sh
VII	805 vs	810 s	810 s
VIII	....	803 vs	802 vs
IX	778 vs	777 w	777 w
X	625 m	648 w	648 w
XI	....	515 w	514 w
XII	442 m	457 m	457 m
XIII	345 m	353 vw	352 vw
XIV	268 w	283 vs,br	280 s,br

*The assignments are: s, strong; vs, very strong; w, weak; vw, very weak; m, medium; sh, shoulder; br, broad.

complexes. All these data suggest that naphthyridines are coordinated monodentately to the copper ion in $Cu(DmNN)_2Cl_2$ and $Cu(dmNN)_2Br_2$ complexes.

The X-ray powder photographs of blue $Cu(dmNN)_2Cl_2$, brown $Cu(dmNN)_2Cl_2$, and olive-green $Cu(dmNN)_2Br_2$ were all similar and did not show any significant changes in the intensity or position of the spectral lines, which indicates that all compounds are isomorphic, in good agreement with the infrared data. The nature of the color change from blue to brown upon exposure to sunlight of the $Cu(dmNN)_2Cl_2$ is a very interesting problem but has not been investigated in this research. The $Cu(dmNN)_2Br_2$ complex gave a magnetic moment of 1.99 B.M. similar to the values obtained for mononuclear copper(II) complexes (see Table VI).

The sparing solubilities of the above complexes in organic solvents did not permit visible spectra measurements. The molar conductivity values of the complexes in DMF solutions indicated that the complexes were not ionic. This suggests coordination of the chloride and bromide ions to the copper ions.

From infrared absorption spectra, magnetic moments, and X-ray powder data it is not possible to assign a certain geometry to the complexes, but a molecular model shows that the methyl groups on the substituted naphthyridine molecules would not permit formation of a cis square-planar geometry around the copper atom. The model shows a

severely hindered structure for a cis complex, whereas this hindrance does not prohibit the molecule from forming a cis geometry in $Cu(NN)_2Cl_2$; therefore a trans geometry is predicted in 2,7-dimethyl substituted naphthyridine complexes. The differences in color of green $Cu(dmNN)_2Br_2$ from $Cu(NN)_2Br_2$ and the similarity of the color to the trans-$Cu(py)_2Br_2$ (green) indicates that the environment of the copper(II) ion should be similar to that of the pyridine complex, i.e., trans geometry rather than cis. The $Cu(dmNN)_2Cl_2$ (blue) also has a different color from that of $Cu(NN)_2Cl_2$ (green) and is similar to trans-$Cu(py)_2Cl_2$ (greenish-blue) which again suggests a trans geometry for the $Cu(dmNN)_2Cl_2$ complex. These observations are in good agreement with the molecular model suggested above.

$Co(NN)_2Cl_2$:— The visible spectrum of $Co(NN)_2Cl_2$ in nitromethane solution showed four broad bands in the region 17000-15000 cm^{-1} (Table IX) with molar absorptivities of 350-420. This is in good agreement with those reported for other tetrahedral cobalt(II) complexes (49). The absorption bands reported for tetrahedral tetrahalocobalt(II) ions have been reported in the range 23000-15000 cm^{-1} (50). The blue complex is stable in nitromethane solution, but not in water or absolute methanol. After dissolving the blue compound in water or absolute methanol a pink solution is obtained which indicates that the compound has different molecular structure in various solvents.

The infrared absorption bands in $Co(NN)_2Cl_2$ are similar to the $Cu(NN)_2Br_2$ spectrum in which bidentate coordination of the ligand was suggested. Three bands at 310(s), 285(m), and 257(m) are observed in the $Co(NN)_2Cl_2$ spectrum which could be assigned to the cobalt-chlorine or cobalt-nitrogen stretching frequencies. Inskeep (51) has reported that the metal-nitrogen stretching frequencies for cobalt(II) copper(II), and zinc(II) complexes of phen and bipy occur in the region 300-264 cm^{-1}, but the infrared spectra of $Co(NN)_4(ClO_4)_2 \cdot 4H_2O$ and $Co(NN)_2NO_3)_2$ complexes (Tables VII and XVIII) showed no bands in this region except modified ligand bands. This indicates that the bands observed in the $Co(NN)_2Cl_2$ are cobalt-chlorine stretching vibrations. This is also in agreement with the low conductivity value of the complex which again suggests coordination of the chlorine atoms.

Banister et al. (52) have reported the preparation and characterization of a compound $Co[(C_6H_5)_3PO]_2(NO_3)_2$ and from the magnetic data (4.69 B.M.) they assigned a tetrahedral structure for the complex. Later, the molecular structure determination of the complex by X-ray studies showed that the cobalt(II) was surrounded by an irregular arrangement of six oxygen atoms, each nitrate ion serving as a bidentate ligand (10).

Although the magnetic data and the visible bands suggest a tetrahedral geometry for the $Co(NN)_2Cl_2$, the infrared spectrum indicates that the naphthyridine molecules are coordinated through both nitrogens

to the cobalt(II) ion. The conductivity value is indicative of non-ionic species and the infrared data support coordination of the chloride ions to the cobalt atom. This means that the cobalt atom is surrounded by four nitrogens from two naphthyridine molecules and two chlorine atoms. The complex is therefore hexacoordinate, but octahedral geometry seems unlikely in view of the tetrahedral appearance of the visible spectrum. Trigonal prismatic geometry is possible in this case and can be correlated with the visible spectrum in the following way. The two coordinating groups on naphthyridine are much closer together than is usual in chelate molecules, and may be considered in this case as a "slightly split" single group. If two of the legs of a trigonal prism are fused in this way an approximate tetrahedron results. It is therefore suggested that this complex exhibits trigonal prismatic coordination, treating the two nitrogens in each naphthyridine molecule as separate coordinating groups, but that the proximity of the two nitrogens leads to a quasi-tetrahedral environment for the cobalt atom, thus accounting for the visible spectrum.

The ultraviolet absorption spectra of halide complexes in absolute methanol solutions are reported in Table XII. Comparison of the coordinated and free ligand spectra showed that there were no significant shifts in the position of the bands although a few extra shoulders were observed in $Cu(NN)Cl_2$ and $Cu(NN)Br_2$ spectra. These data were

Table XII

ULTRAVIOLET ABSORPTION SPECTRA *

λ, nm	ν, kK	ϵ_{max}, $M^{-1}K$	λ, nm	ν, kK	ϵ_{max}, $M^{-1}K$
	$Cu(NN)Cl_2$			$Cu(NN)Br_2$	
308	32.5	6360	308	32.5	7560
(303)	(33.0)	6130	(304)	(32.9)	7310
302	33.1	6610	302	33.1	7750
296	33.8	6180	(296)	(33.8)	7930
(290)	(34.5)	5370	(291)	(34.4)	5590
(284)	(35.2)	4840	(285)	(35.1)	4260
(264)	(37.9)	6270	(261)	(38.3)	5590
261	38.5	6340	257	38.9	5720
(258)	(38.8)	6240	(251)	(39.8)	5470
	$Cu(NN)_2Cl_2$			$Cu(NN)_2Br_2$	
309	32.4	12060	308	32.5	11550
301	33.2	12770	(303)	(33.0)	11200
(297)	(33.7)	11570	301	33.2	12090
(290)	(34.5)	9370	(296)	(33.8)	10840
(285)	(35.1)	7880	(290)	(34.5)	8530
258	38.8	11070	(284)	(35.2)	6750
			257	38.9	10130
	$Co(NN)_2Cl_2$			$C_8H_6N_2$	
308	32.5	20550	309	32.4	5700
301	33.2	21600	(304)	(32.9)	5280
(299)	(33.4)	20490	301	33.2	5900
(296)	(33.8)	19140	(297)	(33.7)	5200
(289)	(34.6)	14640	(290)	(34.5)	4000
(283)	(35.3)	10890	(283)	(35.3)	2900
258	38.8	15900	257	38.9	4310

Table XII (continued)

λ, nm	ν, kK	ϵ_{max}, $M^{-1}K$
	$Cu(dmNN)_2Cl_2$	
317	31.5	22250
309	32.4	18300
303	33.0	18100
(297)	(33.7)	13100
(291)	(34.4)	10400
(285)	(35.1)	7700
254	39.4	9400
	$Cu(dmNN)_2Br_2$	
317	31.5	20600
309	32.4	17250
303	33.0	17000
(297)	(33.7)	11900
(290)	(34.5)	9100
(285)	(35.1)	6350
(257)	(38.9)	5000
(239)	(41.8)	17000
	$C_{10}H_{10}N_2$	
315	31.7	9200
308	32.5	8760
304	32.9	8700
(297)	(33.7)	6070
(291)	(34.4)	4400
(285)	(35.1)	3000
(272)	(36.8)	2600
253	39.5	3800

* Parentheses represent shoulders; absorptions were measured in absolute methanol solutions.

not used in any of the structural analyses but are reported here for future reference.

SUMMARY OF PART I:

Two complexes, $Cu(NN)Cl_2$ and $Cu(NN)Br_2$, have been isolated. The data analyzed indicate that these compounds have the same structure, probably a binuclear 1,8-naphthyridine-bridged complex with at least one and probably both halides coordinated.

The complexes $Cu(dmNN)_2Cl_2$ and $Cu(dmNN)_2Br_2$ have been synthesized. The data obtained indicate coordination of the naphthyridine molecules through one of the nitrogen atoms. A tetra coordinated copper(II) ion (two nitrogens and two halide ions) with trans geometry for these complexes has been suggested.

The infrared spectra of $Cu(NN)_2Br_2$ and $Cu(NN)_2Cl_2$ previously prepared by Enwall were examined. The spectrum of the chloride for which the structure is known was used as a reference point in comparisons of data on the other compounds. The bromide appears from the data to contain chelated naphthyridines and a distorted octahedral geometry.

Finally, the $Co(NN)_2Cl_2$ complex was prepared. The data suggest a trigonal prismatic geometry for the complex with the naphthyridines chelated and chloride ions coordinated.

Three coordination types for 1,8-naphthyridine and its derivatives are clearly distinguishable in this group of compounds: monodentate, as in $Cu(NN)_2Cl_2$ and in the dmNN complexes; bidentate and chelated to a single metal atom as in $Cu(NN)_2Br_2$ and $Co(NN)_2Cl_2$; and syn-syn bidentate, bridging two adjacent metal atoms as in $Cu(NN)Cl_2$ and $Cu(NN)Br_2$.

PART II. PERCHLORATE COMPLEXES:

Syntheses of perchlorate complexes from aqueous solutions resulted in isolation of three tetrakis 1,8-naphthyridine tetrahydrate compounds of manganese(II), cobalt(II), and nickel(II). Two anhydrous tetrakis compounds, $Cu(NN)_4(ClO_4)_2$ and $Zn(NN)_4(ClO_4)_2$, were obtained, and two compounds of formula $Zn(NN)_2(ClO_4)_2 \cdot 4\,H_2O$ and $Ag(NN)ClO_4$. Recrystallization of the copper(II) complex from a mixture of water and acetone gave a crystalline tetrahydrate complex suitable for X-ray data collection.

The analytical and physical data for perchlorate complexes are given in Table III. The molar conductivity measurements of the compounds in nitromethane or absolute methanol solutions exhibit conductivity values appropriate for three-ion species of the first row transition metal complexes and a two-ion species for the silver(I) compound.

The infrared absorption spectra of the complexes were recorded in the region 4000-250 cm^{-1}. The selected ligand modes which change upon coordination are listed in Table XIII. The spectra of all complexes, apart from $Ag(NN)ClO_4$, are identical and there were no significant differences from the spectra of the anhydrous compounds, except the loss of the oxygen-hydrogen stretching band in the region 3500-3100 cm^{-1}. The spectra of the hydrated compounds did not contain any absorption bands at 700 cm^{-1} or 575 cm^{-1} (26,53) which can be assigned to coordinated water vibration frequencies. This indicates that the

Table XIII

SELECTED INFRARED ABSORPTIONS (4000-250 CM^{-1}) OF PERCHLORATE COMPLEXES *

Band	NN	$Mn(NN)_4(ClO_4)_2 \cdot 4H_2O$	$Co(NN)_4(ClO_4)_2 \cdot 4H_2O$	$Ni(NN)_4(ClO_4)_2 \cdot 4H_2O$
I		3500 vs,br	3100 vs,br	3300 vs,br
II	1602 vs	1607 vs	1605 vs	1605 vs
III	1555 vs	1575 s	1572 s	1565 s
IV	1492 vs	1494 vs	1494 vs	1503 vs
V	1228 s	1238 s	1237 s	1242 m
VI		1085 vs,br	1085 vs,br	1090 vs,br
VII	835 vs	835 vs	835 vs	835 s
VIII	809 vs	803 vs	800 vs	805 vs
IX	773 m, sh	778 vs	782 vs	782 m
X	760 vs	762 s,sh	760 s	770 m
XI	483 m, sh	...	...	480 w
XII	475 s	470 s	462 m	468 m
XIII	402 s	405 m	405 m	420 m

Table XIII (continued)

Band	$Cu(NN)_4(ClO_4)_2 \cdot 4H_2O$	$Zn(NN)_4(ClO_4)_2$	$Zn(NN)_2(ClO_4)_2 \cdot 4H_2O$	$Ag(NN)ClO_4$
I	3600 vs,br	....	3500 s,br	....
II	1605 vs	1605 vs	1605 vs	1605 vs
III	1565 s	1570 s	1565 s	1570 s
IV	1492 s	1500 vs,br	1505 vs	1505 vs
V	1240 m	1238 s	1238 s	1240 m
VI	1090 vs,br	1110 vs,br	1095 vs,br	1085 vs,br
VII	838 vs	838 vs	842 vs	855 s
VIII	805 vs	805 vs	837 s	835 vs
IX	785 s	780 vs	800 vs	802 vs
X	760 m	760 s	780 vs	775 s
XI	470 w	475 vw	475 m,sh	490 vw
XII	460 w	470 m	470 m	475 m
XIII	415 w	405 m	425 m	420 m

* The assignments are: s, strong; vs, very strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

water molecules exist as lattice water in the crystals. The similarity of the hydrated and anhydrous spectra (Figure 10) indicates that the naphthyridine coordination is very similar in the two series. The loss of water in the hydrated compounds at room temperature indicates that the water molecules are not tightly bound in the crystals, and hence uncoordinated, further supporting the infrared data. The infrared spectra of these compounds are also identical with the spectrum of anhydrous $Cu(NN)_4(ClO_4)_2$, which is isomorphic with $Fe(NN)_4(ClO_4)_2$ (1) in which the naphthyridines are chelated to the iron atom (Figure 3). The similarity of the infrared spectra, as well as the similarity of the visible spectra, suggests that the naphthyridines are coordinated through both nitrogens to the metal ions in the entire series of hydrated and anhydrous perchlorate complexes. The silver complex is an exception which will be discussed in a separate paragraph.

The perchlorate ion infrared bands in all perchlorate complexes are similar to the free ion bands and there is no indication that perchlorate ion is coordinated to the central metals.

The diffuse-reflectance spectra of cobalt(II), nickel(II), and copper(II) complexes are listed in Table XIV. The positions of the bands are very similar to those reported for octahedral complexes (7,50, 54). The bands for the anhydrous complexes, tetrahydrate complexes, and metal perchlorate hexahydrates are listed for comparison. The diffuse-reflectance spectra of the $Cu(NN)_4(ClO_4)_2 \cdot 4\,H_2O$ and

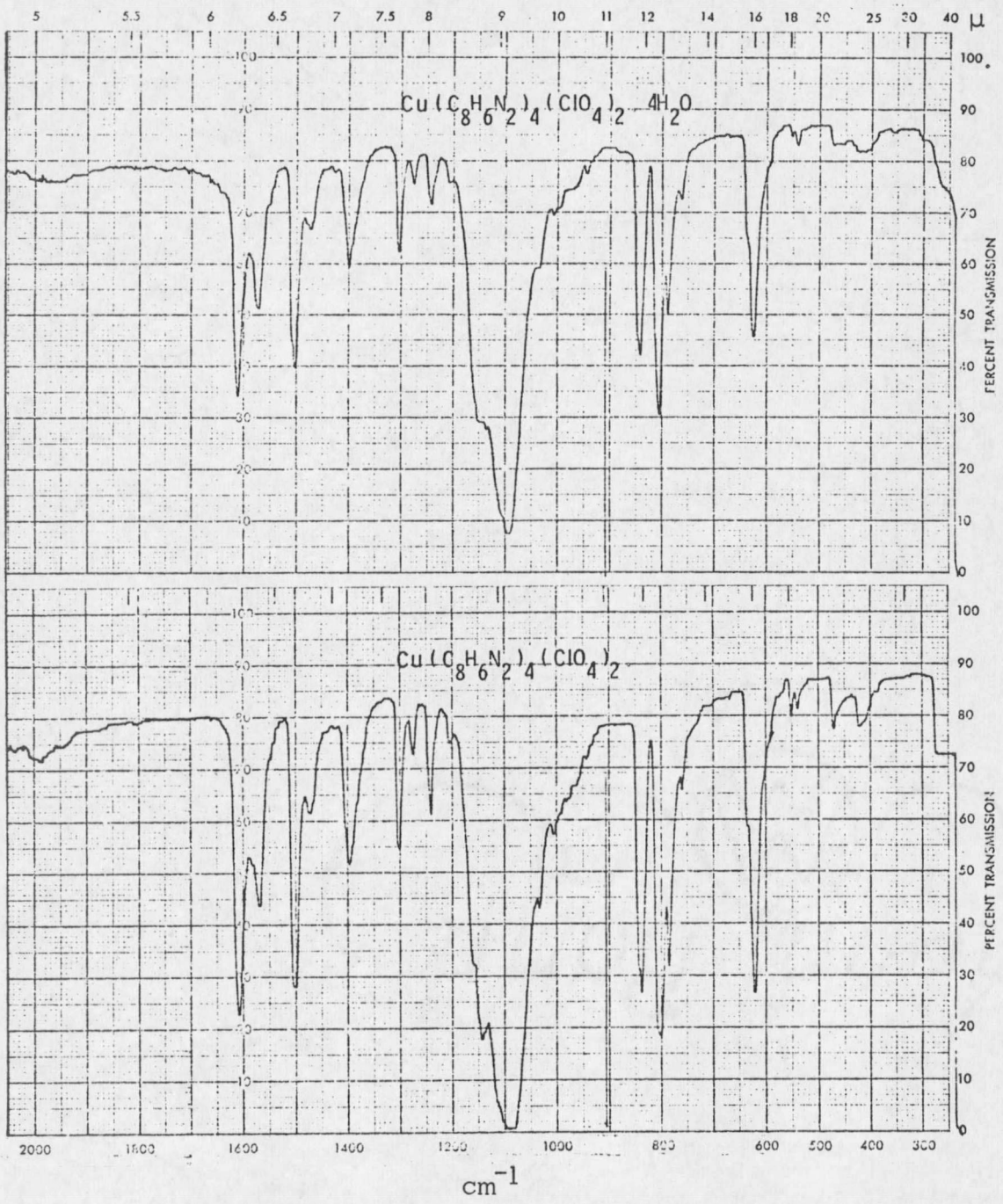


Figure 10. Infrared Spectra of $Cu(C_8H_6N_2)_4(ClO_4)_2 \cdot 4H_2O$ and $Cu(C_8H_6N_2)_4(ClO_4)_2$.

Table XIV

DIFFUSE REFLECTANCE SPECTRA OF PERCHLORATE COMPLEXES (CM^{-1})

Compound	Bands
$Co(NN)_4(ClO_4)_2 \cdot 4H_2O$	28200 sh, 25300 sh, 21400, 20000
$Co(NN)_4(ClO_4)_2$	24400 w, 20600 sh, 18900, 16700 sh
$Co(ClO_4)_2 \cdot 6H_2O$	25000 sh, 21300 sh, 19700
$Ni(NN)_4(ClO_4)_2 \cdot 4H_2O$	26000 sh, 15500, 13800 sh
$Ni(NN)_4(ClO_4)_2$	16300
$Ni(ClO_4)_2 \cdot 6H_2O$	25400, 21800 sh, 18900 s, 15400, 14000
$Cu(NN)_4(ClO_4)_2 \cdot 4H_2O$	16800
$Cu(NN)_4(ClO_4)_2$	16700
$Cu(ClO_4)_2 \cdot 6H_2O$	13300

Table XV

ELECTRONIC ABSORPTION SPECTRA
OF PERCHLORATE COMPLEXES (CM^{-1}) *

In acetonitrile solution	Bands
$Mn(NN)_4(ClO_4)_2 \cdot 4H_2O$	2500 sh(10), 24300 sh(7), 23800 sh(5)
$Co(NN)_4(ClO_4)_2 \cdot 4H_2O$	25000 sh(35), 23700 sh(17), 19600 sh(145), 18500 (210), 16700 sh(40)
$Ni(NN)_4(ClO_4)_2 \cdot 4H_2O$	26300 (45), 16150 (17)
$Cu(NN)_4(ClO_4)_2 \cdot 4H_2O$	27250 sh(35), 15750 (80)
In nitromethane solution	
$Mn(NN)_4(ClO_4)_2 \cdot 4H_2O$	26000 (40), 23700 sh(10)
$Co(NN)_4(ClO_4)_2 \cdot 4H_2O$	26800 (100), 19500 sh(250), 18500 (350)
$Ni(NN)_4(ClO_4)_2 \cdot 4H_2O$	26000 (60), 15850 (14)
$Cu(NN)_4(ClO_4)_2 \cdot 4H_2O$	26000 (300), 16100 (125)

* Parentheses represent molar absorptivities.

$Cu(NN)_4(ClO_4)_2$ in the visible region show similar absorption bands with maxima at 16800 cm^{-1} and 16700 cm^{-1} respectively. This again indicated that the geometry of the copper ion in both complexes is identical which is in good agreement with the infrared absorption data. The visible absorption bands of the metal naphthyridine complexes appear at higher frequencies than those of metal perchlorate hexahydrates which indicates that naphthyridine has a higher ligand field strength than water. This is in agreement with earlier work by Hendricker and Bodner (7), who have determined the 10 Dq values of dmNN in the complexes of nickel(II), iron(II), and cobalt(II) with stoichiometry $M(dmNN)_3^{2+}$ and concluded that dmNN has a ligand field strength similar to pyridine.

The solution spectra in acetonitrile and nitromethane of perchlorate complexes of transition metals containing less than ten d electrons are reported in Table XVI. Comparison of the diffuse-reflectance and solution spectra of the complexes shows that the positions of the bands change considerably, indicating that the ligands are coordinated differently in solution. The molar absorptivity of the complexes as well as the band positions change in both acetonitrile and nitromethane solutions which is indicative of the variable coordination ability of the solvent.

Because of the loss of water of hydration in hydrated perchlorate complexes, accurate X-ray powder data were very difficult to collect

with the equipment available. It was decided to obtain X-ray single crystal data by a special procedure in order to protect the compounds from dehydration during the period that the compounds were exposed to the X-ray beam. Therefore, X-ray single crystal data for hydrated manganese(II), cobalt(II), nickel(II), and copper(II) complexes were obtained by mounting the crystal inside a sealed glass capillary containing a small amount of water or mother liquor. The data were collected by Weissenberg methods using CuK_{α} ($\lambda = 1.54\,\mathring{A}$) radiation. Comparison of the film data of the compounds showed that only the complexes of manganese(II) and cobalt(II) were isomorphic, in contrast to data reported in the literature, indicating that all anhydrous tetrakis compounds from manganese(II) to copper(II) were isomorphous. The space group and cell parameters were obtained to verify this unexpected structural variation. Cell dimensions were determined by the methods given by Buerger (55) from rotation and Weissenberg photographs. The film data indicated that all complexes crystallized in monoclinic cells cells except the nickel(II) complex, which crystallized in a triclinic cell. Cobalt(II) and manganese(II) complexes were isomorphic, as noted above. The crystallographic data for all monoclinic complexes are listed in Table XVI. The crystal density of the copper(II) complex, $D_m = 1.52\ gcm^{-3}$, measured by flotation, indicated that there are four molecules in the unit cell. Clearfield et al. (3) have reported two molecules per unit cell for the $Fe(NN)_4(ClO_4)_2$ which was isomorphous

Table XVI

CRYSTALLOGRAPHIC DATA OF PERCHLORATE COMPLEXES

Compound	Space Group	β angle	a(Å)	b(Å)	c(Å)
$Cu(NN)_4(ClO_4)_2 \cdot 4H_2O$	C_c or $C_{2/c}$	~88°	15.83	11.55	17.06
$Mn(NN)_4(ClO_4)_2 \cdot 4H_2O$	$C_{2/m}$, C_2 or C_m	~90°	15.85	12.90	8.45
$Co(NN)_4(ClO_4)_2 \cdot 4H_2O$	$C_{2/m}$, C_2 or C_m	~90°	15.85	12.90	8.45
$Zn(NN)_4(ClO_4)_2$	$P2_{1/c}$	~89°	17.05	11.16	16.40

with the corresponding copper(II) compound. The iron(II) complex crystallized in a triclinic cell with space group $P\bar{1}$. The work of Bodner and Hendricker (1) with anhydrous tetrakis 1,8-naphthyridine complexes indicated that the structures of all compounds from manganese(II) to copper(II) were identical, and zinc(II) was very similar. Our data confirm the isomorphism on $Cu(NN)_4(ClO_4)_2$ and $Co(NN)_4(ClO_4)_2$ and indicate that $Zn(NN)_4(ClO_4)_2$ does indeed have a somewhat different structure. The zinc(II) complex crystallizes in a monoclinic cell with space group $P2_{1/c}$ and β angle of 89° which is in contrast to the powder data reported earlier, although crystallization from aqueous solution may have influenced the character of the crystal. The β angle measured and calculated from zero level Weissenberg photographs gave a value of 88-90° for all complexes.

Some additional information about the geometry of the cation can be obtained from these data. The multiplicity of the general position in $C_{2/m}$ or $C_{2/c}$ is eight-fold; that of the general position in C_2, C_c, or C_m is four-fold. The density measurements of $Cu(NN)_4(ClO_4)_2 \cdot 4\,H_2O$ indicates that there are four molecules per unit cell. Since the similarity in cell dimensions to the cobalt and manganese compounds suggests a close structural similarity one can deduce that the number of molecules per unit cell should be two in these latter cases. If in these two compounds (cobalt and manganese) the space group is $C_{2/m}$, the complex would then be required to have 2/m symmetry. In view of the demonstrated similarity of their infrared spectra to that of $Fe(NN)_4(ClO_4)_2$, which does not even approach 2/m symmetry, this seems unlikely. In C_m or C_2 the complex would be required to have 2 or m symmetry, both of which are approached by the iron complex. Since the same symmetry is required of the complex by the space group in these two complexes, and since the similarity in cell dimensions suggests a similar structure to $Cu(NN)_4(ClO_4)_2 \cdot 4\,H_2O$, it seems probable that copper lies on special positions in this compound, which would require that $C_{2/c}$ acentric space group be the correct one. Centric compounds are easier to study than acentric, and monoclinic is generally easier than triclinic; hence a structure determination on the copper compound seems likely to yield better data on the coordination geometry than was obtained from the determined iron complex.

The anhydrous zinc complex appears to have four molecules per unit cell, from comparisons of the cell dimensions, and hence one molecule in a general position. The comparative ease of determination in a monoclinic space group compared to a triclinic one suggests that this may also be a good compound for structure study.

$Zn(NN)_2(ClO_4)_2 \cdot 4\,H_2O$:— The infrared spectrum of $Zn(NN)_2(ClO_4)_2 \cdot 4\,H_2O$ is similar to those of the other hydrated tetrakis complexes. There is no indication that perchlorate anions or water molecules are coordinated to the zinc(II) ion. The similarity of the infrared absorption bands suggests that the naphthyridines are coordinated through two nitrogens to the central metal. This suggests that zinc(II) ion is surrounded by four nitrogen atoms. Since tetrahedral geometry for four coordination is usual for zinc(II), a tetrahedral arrangement for this complex is suggested.

$Ag(NN)ClO_4$:— The spectrum of the $Ag(NN)ClO_4$ complex is different from those of the tetrakis and <u>bis</u> perchlorate complexes. The ligand bands are similar to the spectrum of the $Cu(NN)_2Cl_2$ in which naphthyridines are coordinated through one of the nitrogens to the copper atom. The perchlorate bands are identical to the free anion bands which indicates that the perchlorate ion is not coordinated to the silver(I) ion. However the data obtained for this complex is insufficient to suggest any possible geometry for the coordination to the silver(I) ion.

The ultraviolet absorption bands of the complexes in absolute methanol solutions and their molar absorptivities are listed in Table XVII. Comparison of the free and coordinated ligand bands shows no significant shifts in the positions of any of the bands, although a few extra shoulders appear in the complexes. The free ligand band at 38900 cm^{-1} appears at a somewhat lower frequency, 37700 cm^{-1} in the silver(I) compound, but the significance of this shift is unclear at present.

SUMMARY OF PART II.

Tetrakis perchlorate complexes of manganese(II), cobalt(II), nickel(II), and copper(II) with 1,8-naphthyridine of the general formula $M(NN)_4(ClO_4)_2 \cdot 4\,H_2O$ have been prepared. From comparison of the data with those of anhydrous tetrakis compounds reported in the literature, chelation of the ligand was established in all cases. All these complexes crystallized in monoclinic cells except the nickel(II) compound which is triclinic.

Zinc(II) ion forms a bis complex, $Zn(NN)_2(ClO_4)_2 \cdot 4\,H_2O$. The similarity of the ligand chelation with the tetrakis hydrated compounds is discussed. Dodecahedral geometry for the tetrakis complexes and tetrahedral geometry for $Zn(NN)_2(ClO_4)_2 \cdot 4\,H_2O$ has been proposed.

Table XVII

ULTRAVIOLET ABSORPTION SPECTRA *

λ, nm	ν, KK	ε_{max}, $M^{-1}K$	λ, nm	ν, kK	ε_{max}, $M^{-1}K$
$Mn(NN)_4(ClO_4)_2 \cdot 4\,H_2O$			$Co(NN)_4(ClO_4)_2 \cdot 4\,H_2O$		
307	32.6	22700	308	32.5	22500
301	33.2	23800	300	33.3	25100
(296)	(33.8)	20900	(295)	(33.9)	20900
(290)	(34.5)	17100	(290)	(34.5)	16400
(283)	(35.3)	11700	(283)	(35.5)	11800
(272)	(36.8)	12300	(276)	(36.2)	10900
(269)	(37.2)	13700	(271)	(36.9)	13000
(264)	(37.9)	15700	(263)	(38.0)	16100
257	38.9	17400	258	38.7	17300
$Ni(NN)_4(ClO_4)_2 \cdot 4\,H_2O$			$Cu(NN)_4(ClO_4)_2 \cdot 4\,H_2O$		
307	32.6	22300	308	32.5	38300
301	33.2	23400	300	33.3	40400
(297)	(33.7)	20600	(295)	(33.9)	35300
(289)	(34.6)	15800	(290)	(34.5)	28400
(283)	(35.3)	11800	(283)	(35.3)	21200
(277)	(36.1)	10700	(274)	(36.5)	21700
(272)	(36.8)	12200	(269)	(37.2)	25400
(269)	(37.2)	13400	258	38.7	30000
257	38.9	17300			

Table XVII (continued)

λ, nm	ν, kK	ϵ_{max}, $M^{-1}K$
	$Zn(NN)_4(ClO_4)_2$	
307	32.6	22900
300	33.3	24000
(295)	(33.9)	21100
(289)	(34.5)	15800
(284)	(35.2)	12100
(274)	(36.5)	11400
(270)	(37.0)	13200
258	38.8	17600
	$Zn(NN)_2(ClO_4)_2 \cdot 4\,H_2O$	
308	32.5	10700
301	33.2	11250
(296)	(33.8)	9870
(289)	(34.6)	7300
(284)	(35.2)	5370
(276)	(36.2)	5230
(271)	(36.9)	6120
259	38.6	8010
	$Ag(NN)ClO_4$	
309	32.4	6100
300	33.3	6300
(296)	(33.8)	5900
(291)	(34.4)	4200
(285)	(35.1)	4000
(270)	(37.0)	4600
265	37.7	4800

* Parentheses designate shoulders.

A silver compound, $Ag(NN)ClO_4$, has been isolated and from the infrared data monodentate coordination of the ligand has been tentatively assigned.

The anhydrous tetrakis complexes previously reported have been prepared for comparison, and the structural data for these compounds has been confirmed and expanded.

PART III. NITRATE COMPLEXES

Transition metal nitrate complexes of 1,8-naphthyridine were isolated either from aqueous or organic solutions. Cobalt(II) and zinc(II) form tetrakis hexahydrates; manganese(II), cobalt(II), and copper(II) form anhydrous bis complexes; and nickel(II), copper(II), and zinc(II) form complexes of unique stoichiometry. X-ray single crystal data indicates that the two hexahydrates are not isomorphic, and the anhydrous bis compounds also exhibit entirely different crystal structures.

The analytical and physical data on nitrate complexes are given in Table IV. The molar conductivities of all the complexes were determined in absolute methanol solutions. The values indicate a three-ion species for all first row transition metal complexes and a two-ion species for the silver(I) compound. These compounds therefore appear to ionize completely in solution although several of them contain coordinated nitrate ion, as will be discussed below.

$Cu(NN)_4(NO_3)_2 \cdot 6\,H_2O$ and $Zn(NN)_4(NO_3)_2 \cdot 6\,H_2O$:— The infrared absorption bands of the complexes are listed in Table XVIII. The assignments of the ligand bands are those reported in the literature (37). The bands IV, V, and XIV are characteristic of nitrate ion. The spectra of these compounds showed splitting of the ligand band at 1128 cm^{-1} to two bands at 1128 cm^{-1} and 1147 cm^{-1}. This splitting of the ligand band is observed only in complexes containing naphthyridine molecules coordinated through both nitrogen atoms as has been

Table XVIII

SELECTED INFRARED ABSORPTIONS (4000-250 CM^{-1}) OF NITRATE COMPLEXES *

Band	NN	$Ni(NN)_2(NO_3)_2 \cdot 4H_2O$	$Co(NN)_4NO_3)_2 \cdot 6H_2O$	$Zn(NN)_4(NO_3)_2 \cdot 6H_2O$	$Ag(NN)NO_3$
I		3300 vs,br	3400 vs,br	3400 vs,br	....
II	1555 s	1580 s	1570 s	1565 s	1572 s
III	1492 vs	1507 vs	1502 vs	1500 vs	1500 vs
IV	....	1390 vs,br	1395 vs,br	1390 vs,br	1385 vs,br
V	....	....	....	....	....
VI	1275 m	1275 m	1280 w	1275 w	1270 m
VII	1228 s	1240 s	1240 m	1240 m	1235 m
VIII	....	1147 m	1150 m	1150 m	....
IX	1045 s	1068 s	1068 s	1068 s	1060 vw
X	1027 m	1045 s	1040 w	1035 w	1032 w
XI	985 w	995 s	980 vw	975 vw	...
XII	970 w	975 vs	965 vw	960 w	...
XIII	953 w	948 s	945 vw	...	...
XIV	...	827 s	830 s	828 s	825 s
XV	772 w,sh	782 s	785 s	783 s	...
XVI	760 s	772 s	762 m	760 s	772 s
XVII	...	690 vs	...	...	...
XVIII	600 w	630 m	630 w	630 w	...
XIX	...	575 vs	...	...	...
XX	400 m	420 m	405 w	405 w	410 vw

Table XVIII (continued)

Band	NN	$Mn(NN)_2(NO_3)_2$	$Co(NN)_2(NO_3)_2$	$Cu(NN)_2(NO_3)_2$	$Cu(NN)_{2.16}(NO_3)_2$
I					
II	1555 s	1585 s	1580 s	1575 m	1570 m
III	1492 vs	1500 vs	1505 vs	1503 vs	1505 vs
IV	....	1390 vs,br	1385 vs,br	1380 vs,br	1390 vs,br
V	....	1315 vs	....	....	....
VI	1275 m	1265 vs	1270 s,sh	1268 s	1270 vw
VII	1228 s	1238 s	1238 s	1242 m	1240 m
VIII	....	1135 s,sh	1147 s	1145 m,sh	1150 m
IX	1045 s	1065 w	1065 s	1060 m	1065 m
X	1027 m	1035 s	1032 m	1018 s	1038 w
XI	985 w	...	...	...	975 vw
XII	970 w	...	...	...	960 vw
XIII	953 w	958 w	958 w	...	...
XIV	...	828 s	825 s	810 s	830 s
XV	772 w,sh	780 s	782 vs	785 vs	787 s
XVI	760 s	740 w	...	748 vw	...
XVII	...	...	...	...	...
XVIII	600 w	642 m	628 m	625 vw	630 w
XIX	...	555 m	550 w	550 vw	550 w
XX	400 m	415 w	425 m	422 w	420 m

*The assignments are: s, strong; vs, very strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder.

discussed in earlier sections of this thesis. This indicates that the naphthyridines are chelated in these compounds to the cobalt(II) and zinc(II) ions. The spectra of the above complexes are superimposable on the ligand bands of the corresponding metal perchlorate complexes, except for the nitrate and perchlorate anion bands, which also supports the above conclusion. The nitrate ion bands are similar to those of free anion, indicating that nitrate ions are not coordinated.

The diffuse-reflectance spectrum of $Co(NN)_4(NO_3)_2 \cdot 6\,H_2O$ (Table XIX) is very similar to the corresponding perchlorate complex, $Co(NN)_4(ClO_4)_2 \cdot 4\,H_2O$ (Table XV) in the visible region which again suggests chelation of the ligand and a dodecahedral geometry for the metal ion in both of these complexes similar to that in the perchlorate compounds.

$Ni(NN)_2(NO_3)_2 \cdot 4\,H_2O$:— The infrared spectrum of the $Ni(NN)_2(NO_3)_2 \cdot 4\,H_2O$ complex showed significant differences when compared with that of the perchlorate complex. Some new intense bands were observed at 995(s), 975(vs), and 575(vs) cm^{-1}. These bands were not observed in 1,8-naphthyridine complexes discussed in the earlier part of this thesis, which suggests a different coordination geometry for this complex. The two very strong bands in the nickel(II) complex spectrum at 690 cm^{-1} and 575 cm^{-1} are indicative of coordinated water (26,56). None of the other compounds prepared in this work show any evidence of coordinated water. This complex appears to be unique.

Table XIX

REFLECTANCE SPECTRA OF NITRATE COMPLEXES (CM^{-1})

Compound	Bands
$Co(NN)_2(NO_3)_2$	25600 sh, 24100 w, 20800, 19800, 18700 sh
$Co(NN)_4(NO_3)_2 \cdot 6\,H_2O$	25300 w, 21500, 20000
$Co(NO_3)_2 \cdot 6\,H_2O$	25000 sh, 21700 sh, 20000, 16700 sh
$Cu(NN)_{2.16}(NO_3)_2$	25000 sh, 24000 sh, 15900
$Cu(NO_3)_2 \cdot 3\,H_2O$	16100 sh, 14300, 13200 sh
$Ni(NN)_2(NO_3)_2 \cdot 4\,H_2O$	25300 sh, 23800 sh, 15700, 13900 sh
$Ni(NO_3)_2 \cdot 6\,H_2O$	25800, 22200 sh, 18900 sh, 15900, 14200

The nitrate bands are identical to the free ion bands, indicating that nitrate ions are not coordinated. The ligand bands are similar to the spectra of tetrakis cobalt(II) and zinc(II) nitrate complexes which were discussed earlier, suggesting that the naphthyridines are chelated to the nickel atom.

Comparison of the diffuse-reflectance spectrum of the $Ni(NN)_2(NO_3)_2 \cdot 4\,H_2O$ complex with that of $Ni(NO_3)_2 \cdot 6\,H_2O$ (Table XIX) suggests that the geometry of the nickel(II) ion is octahedral. From the infrared spectrum it is not possible to decide whether two or four water molecules are coordinated to the nickel atom. But since the naphthyridines are chelated to the central metal, it seems likely that there are two coordinated water molecules and two chelated naphthyridines in an

octahedral arrangement. Coordination of four water molecules to give a dodecahedral geometry cannot be ruled out.

$Mn(NN)_2(NO_3)_2$ and $Cu(NN)_2(NO_3)_2$:— The ligand bands in the infrared spectra of these two compounds are superimposable on tetrakis nitrate complexes, which suggests chelation of the naphthyridine molecules to the metal ions. However the nitrate ion bands are similar to those reported for bidentate nitrate ions (49,57). When free nitrate ion, symmetry D_{3h}, coordinates to the central metal its symmetry is lowered to C_{2v} (covalently bound through one or two oxygens). Cotton et al. (44) have reported the infrared bands for several nitrate complexes containing nitrate coordinated through two oxygen atoms. Gatehouse et al. (58) have studied nitrate complexes in which the nitrate ions are covalently bonded through one oxygen atom and have assigned the infrared active bands for the nitrate anion. They have also reported the following assignments (Table XX) for different ranges of observable modes in coordinated nitrates.

Table XX

Bands (cm^{-1})	Assignments
1531-1481	asymmetric stretch
1290-1253	NO_2 symmetric stretch
1034-970	NO stretch
800-781	nonplanar rock

The strong nitrogen-oxygen stretching band appearing in the range 1034-970 cm^{-1} will be observed as a weak band for uncoordinated nitrate anion. The nitrate ion bands of several complexes containing free, monodentate, and bidentate nitrate ions are listed in Table XXI for comparison. The strong band at 1035 cm^{-1} and 1018 cm^{-1} in the manganese(II) and copper(II) complexes, respectively, is indicative of coordinated nitrate ions (Figure 11). This band is observed as a weak band in tetrakis nitrate complexes.

Table XXI

INFRARED ABSORPTION BANDS OF SOME NITRATE COMPLEXES (CM^{-1})

Ionic nitrate:	
$[Co(NH_3)_6](NO_3)_3$	1376 s, 1299 sh, 1045 w, 823 s
Monodentate nitrate:	
$[Co(NH_3)_4(NO_3)_2]$	1499 s, 1393 s, 1348 sh, 1266 s, 1049 w, 1010 s, 825 m, 800 w
$[Ni(PEt_3)_2(NO_3)_2]$	1513 m, 1418 sh, 1359 vs, 1272 s, 1018 s 805 m
Bidentate nitrate:	
$[((CH_3)_3PO)_2Co(NO_3)_2]$	1517 s, 1492 s, 1469 s, 1317 sh, 1304 sh, 1282 s, 1024 m, 812 w
$[Co((C_6H_5)_3PO)_2(NO_3)_2]$	1503 sh, 1497 s,br, 1493 s, 1290 s, 1024 m, 812 w, 808 w

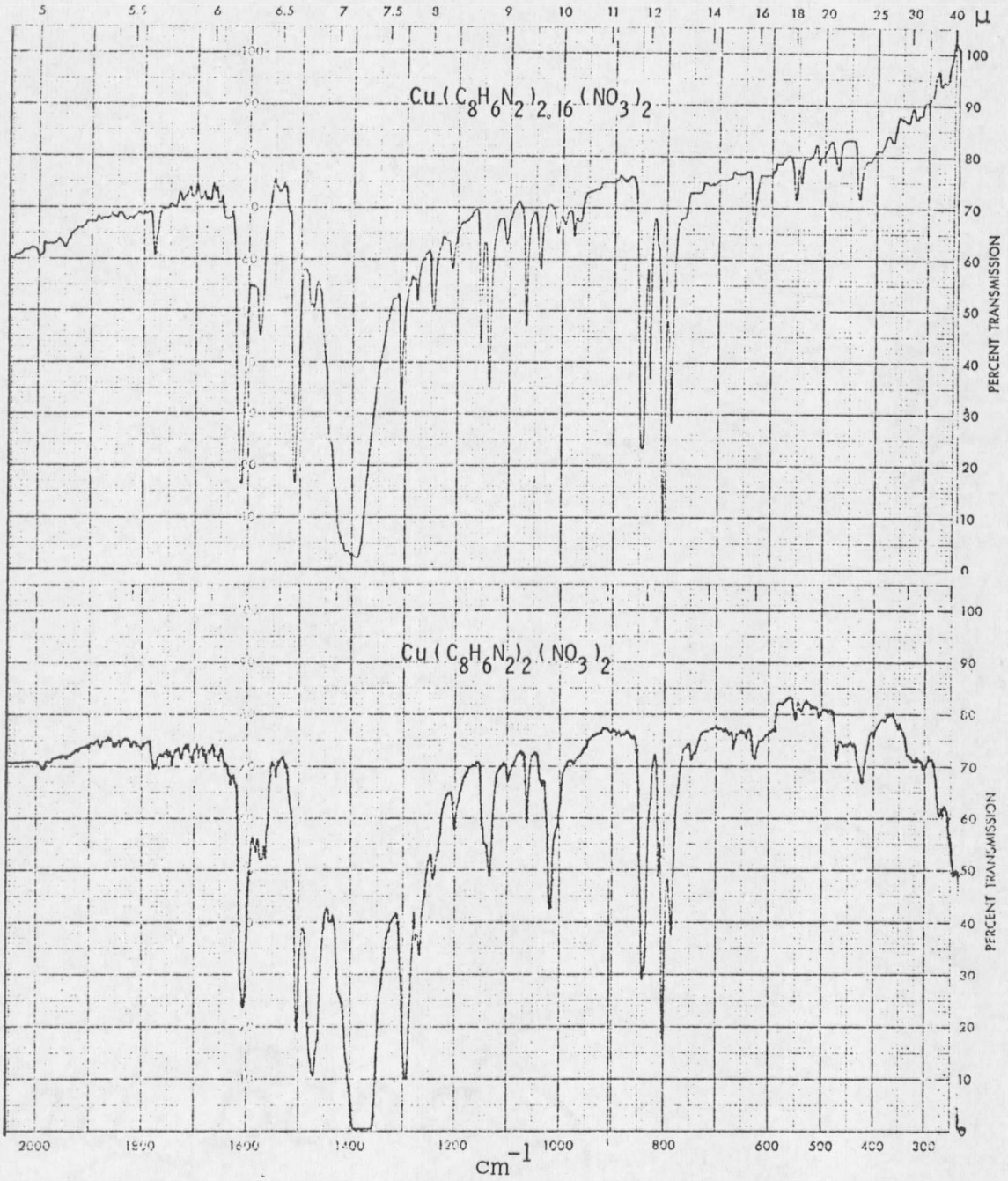


Figure 11. Infrared Spectra of $Cu(C_8H_6N_2)_{2.16}(NO_3)_2$ and $Cu(C_8H_6N_2)_2(NO_3)_2$.

The $Cu(NN)_2(NO_3)_2$ complex had not been prepared at the time the reflectance spectra were obtained and no comparison of the spectra can be made. The solution spectra of both $Cu(NN)_2(NO_3)_2$ and $Cu(NN)_{2.16}(NO_3)_2$ complexes in absolute methanol show an absorption band at 13000 cm^{-1} rather than the 15900 cm^{-1} obtained for the latter compound from its reflectance spectra. This indicates that the molecular structures of the copper(II) compounds are different in the crystal and in solution; therefore the solution spectral data cannot be used for drawing any conclusions about the geometry of the copper atom in the solid. The similarity of the ligand infrared bands to those observed in all tetrakis complexes and the evidence for bidentate coordination of nitrate ions argues for the more familiar dodecahedral geometry. Two naphthyridine molecules are replaced in these cases by nitrate ions.

$Co(NN)_2(NO_3)_2$:— Comparison of the $Co(NN)_2(NO_3)_2$ infrared spectrum with the other nitrate compounds discussed earlier in this section indicates that naphthyridines are again coordinated through both nitrogens to the cobalt atom. However, the nitrate ion bands are similar to nitrate complexes (59) having monodentate coordination. This suggests that cobalt(II) ion is surrounded by four nitrogens from naphthyridine and two oxygens from nitrate ions.

The diffuse reflectance spectrum of this complex (Table XIX) differs from the spectrum of the $Co(NN)_4NO_3)_2 \cdot 6\,H_2O$, in which only naphthyridines are chelated to the cobalt atom, but is similar to that of

the octahedral $[(CH_3)_3PO]_2Co(NO_3)_2$ complex studied by Cotton et al. (59). The absorption bands for the phosphine oxide complex have been reported at 20600, 19000, and 17920 cm^{-1}. The visible absorption bands of the $Co(NN)_2NO_3)_2$ complex listed in Table XX are very similar, suggesting a similar geometry to that of the phosphine oxide complex. From the infrared absorption spectrum it was concluded that the naphthyridines were chelated to the cobalt atom and the nitrate ions were coordinated through one of the oxygen atoms. This will supply six coordination groups for the cobalt(II) ion, and a geometry similar to that of the phosphine oxide complex.

$Cu(NN)_{2.16}(NO_3)_2$:— This complex has an unusual stoichiometry which requires some explanation. One might reasonably suppose that there were in fact only two naphthyridine molecules per copper and that small errors in the analyses were responsible for the derivations. However, this compound has properties different from a second compound (discussed above) with exactly two naphthyridine molecules per copper, and the analyses for all components (copper, carbon, hydrogen, and anion) fit very precisely the reported formula, which gives us a measure of confidence in the chosen formula. The magnetic moment of the complex (1.98 B.M.) suggests that the $Cu(NN)_{2.16}(NO_3)_2$ is mononuclear. The ligand infrared bands (Table XVIII and Figure 11) are similar to all the other nitrates thus far discussed indicating bidentate coordination of the naphthyridines. The nitrate ion bands are similar to free nitrate

ions (Figure 11) which suggests that nitrate ions are not coordinated to the copper(II) ion.

The diffuse-reflectance spectrum of $Cu(NN)_{2.16}(NO_3)_2$ is different from that of the $Cu(NN)_4(ClO_4)_2$ complex which suggests that the geometry of the copper(II) ion is different from that of the perchlorate compound, which is in good agreement with the infrared data. The absorption maxima are similar to those of distorted octahedral copper(II) complexes reported in the literature (46) (see Table X), but the copper(II) electronic absorption bands are so broad that no certain conclusion as to the geometry of this complex can be drawn.

$Ag(NN)NO_3$:— The infrared spectrum of the $Ag(NN)NO_3$ compound shows significant differences from those nitrate complexes of first transition series. The splitting of the ligand band at 1128 cm^{-1} is not observed in $Ag(NN)NO_3$, and splitting of the ligand bands in the region 900-750 cm^{-1} is quite different from the complexes in which chelation of the ligand has been postulated. The spectrum of the silver(I) compounds of both nitrate perchlorates are very similar to that of $Cu(NN)_2Cl_2$ in which naphthyridines were coordinated through one of the nitrogens to the copper(II) ion. The infrared bands for the nitrate anion show the usual characteristics of the free ion spectrum indicating that nitrate ion is not coordinated to the silver(I) ion. The infrared spectrum thus suggests monodentate coordination for the ligand in

$Ag(NN)NO_3$ complex with nitrate ion not coordinated to the silver atom.

The ultraviolet absorption bands of the nitrate compounds in absolute methanol solutions and their molar absorptivities are reported in Table XXII. The positions of the coordinated ligand bands do not change significantly from those of free ligand bands, although there are some extra shoulders observed after complexation. The shapes and positions of the bands are similar to the corresponding perchlorate bands listed in Table X.

SUMMARY OF PART III

The complexes $Co(NN)_4(NO_3)_2 \cdot 6\,H_2O$ and $Zn(NN)_4(NO_3)_2 \cdot 6\,H_2O$ have been synthesized. The data indicate a geometry similar to that of the tetrakis perchlorate complexes.

Bis complexes of manganese(II), cobalt(II), and copper(II) with stoichiometry $M(NN)_2(NO_3)_2$ have been isolated. Analysis of the data indicates that the naphthyridines are chelated in all these complexes; nitrate ions are chelated to manganese(II) and copper(II), but monodentately coordinated in the cobalt(II) complex. Dodecahedral geometry has been suggested for the manganese(II) and copper(II) compounds and octahedral geometry for the cobalt(II) complex.

Table XXII

ULTRAVIOLET ABSORPTION SPECTRA *

λ, nm	ν, kK	ε_{max}, $M^{-1}K$	λ, nm	ν, kK	ε_{max}, $M^{-1}K$
$Mn(NN)_2(NO_3)_2$			$Co(NN)_2(NO_3)_2 \cdot 4\,H_2O$		
309	32.4	10600	309	32.4	11450
(303)	(33.0)	10600	(303)	(33.0)	10930
301	33.2	11200	301	33.2	12030
(296)	(33.8)	9910	(296)	(33.8)	10500
(290)	(34.5)	7660	(290)	(34.5)	8150
(283)	(35.3)	5300	(284)	(35.2)	5850
257	38.9	8100	258	38.8	10200
$Co(NN)_2(NO_3)_2$			$Co(NN)_4(NO_3)_2 \cdot 6\,H_2O$		
309	32.4	6400	309	32.4	15100
(304)	(32.9)	6150	(304)	(32.9)	14500
302	33.1	6800	301	33.2	15850
(296)	(33.8)	5950	(296)	(33.8)	13850
(290)	(34.5)	4500	(290)	(34.5)	10800
(284)	(35.2)	3400	(284)	(35.2)	10150
258	38.8	4800	259	38.6	11150

Table XXII (continued)

λ, nm	ν, kK	ϵ_{max}, $M^{-1}K$	λ, nm	ν, kK	ϵ_{max}, $M^{-1}K$
$Cu(NN)_{2.16}(NO_3)_2$			$Cu(NN)_2(NO_3)_2$		
309	32.4	13050	309	32.4	11300
301	33.2	13650	301	33.2	11900
(297)	(33.7)	12300	(297)	(33.7)	10800
(290)	(34.5)	9600	(290)	(34.5)	8650
(284)	(35.2)	7500	(284)	(35.2)	6750
(274)	(36.5)	7600	(274)	(36.5)	6750
(268)	(37.3)	9250	(268)	(37.3)	8100
(264)	(37.9)	10300	(264)	(37.9)	9050
259	38.6	10600	254	39.4	10400
$Zn(NN)_4(NO_3)_2 \cdot 6\,H_2O$			$Ag(NN)NO_3$		
309	32.4	24000	309	32.4	6200
301	33.2	25150	301	33.2	6450
(297)	(33.7)	22100	(297)	(33.7)	5800
(290)	(34.5)	15900	(290)	(34.5)	4400
(284)	(35.2)	11900	(285)	(35.1)	3620
(273)	(36.6)	11700	(277)	(36.1)	3400
(271)	(36.9)	13150	(273)	(36.6)	3900
259	38.6	17650	260	38.5	5050

* Parentheses represent shoulders.

The compound $Cu(NN)_{2.16}(NO_3)_2$ was prepared from aqueous solution and the data indicate that the naphthyridines are chelated to the copper atom. No certain assignment of structure can be made in this case.

The complex $Ni(NN)_2(NO_3)_2 \cdot 4\,H_2O$ has been synthesized. The data suggest chelation of the ligands with water molecules coordinated. Octahedral or dodecahedral geometry for the nickel(II) ion are possible explanations of the data.

Experiments with silver(I) ion resulted in isolation of an $Ag(NN)NO_3$ complex in which the naphthyridine is coordinated monodentately to the silver atom. The geometry of the coordination complex is not known.

PART IV. COPPER(I) COMPLEXES

In 1970 several tris complexes of 2,7-dimethyl-1,8-naphthyridine with various metals of general formula $M(dmNN)_3ClO_4)_2$, including a brown copper(II) compound, were reported (7). The analysis presented in that report indicated that all complexes contained octahedrally coordinated bidentate naphthyridine. Copper(II) compounds in which the metal atom is surrounded by six nitrogen atoms are normally blue, and the report of a brown copper(II) complex so coordinated was thus rather unusual. Attempts to duplicate the synthesis of this brown material with both NN and dmNN were made. The desired compounds were obtained but cannot be characterized as copper(II) compounds. The two products were analyzed and characterized. Magnetic moments and electronic spectra indicated that both compounds were copper(I) complexes. Moreover, for comparison, copper(I) chloride complexes of naphthyridines were prepared directly from copper(I) chloride and naphthyridines.

Four copper(I) complexes of 1,8-naphthyridine and its 2,7-dimethyl derivative containing chloride and perchlorate anions have been synthesized and characerized in this research. The analytical and physical data are given in Table V. Conductivity measurements on the copper(I) naphthyridine complexes in acetonitrile, nitromethane, or absolute methanol indicate that the complexes in solution are ionic; the value

obtained corresponds to singly ionizing salts, which agrees with results reported earlier for copper(I) complexes (6).

Magnetic susceptibility measurements on the complexes by the Gouy method indicate that the complexes are diamagnetic. Visible and ultraviolet spectra show only charge transfer bands associable with the ligand. These two observations clearly establish the formal oxidation state of the metal in these complexes as +1. The complex $Cu_2(NN)Cl_2$ gave a reproducible melting point at $292 \pm 1^{o}C$. All other compounds in this group decomposed without melting at temperatures at or below $270^{o}C$.

The infrared spectra of the copper(I) compounds are summarized in Table XXIII. Assignments for the ligand bands are given in the literature (37).

$Cu(NN)ClO_4$:— The infrared spectrum of this complex was compared with those of complexes discussed earlier in this thesis. The ligand bands are similar to $Cu(NN)Cl_2$ and $Cu(NN)Br_2$ spectra in which naphthyridines are believed to bridge across two copper(II) ions. This suggests a similar structure for the copper(I) compound. The broad, very strong perchlorate bands at 1115 cm^{-1} and 1087 cm^{-1} (antisymmetric stretch) and the bands at 635(m) cm^{-1} and 622(s) cm^{-1} (antisymmetric bend) are characteristic of coordinated perchlorate (26). When perchlorate ion coordinates its symmetry is lowered from T_d (free ion) to C_{3v} (coordination through one oxygen) or C_{2v} (coordination through two

Table XXIII

SELECTED INFRARED ABSORPTIONS (4000-250 CM^{-1}) OF COPPER(I) COMPLEXES

Band	NN	$Cu(NN)ClO_4$	$Cu_2(NN)Cl_2$	Band	dmNN	$Cu(dmNN)_2ClO_4$	$Cu_2(dmNN)Cl_2$
I	1555 vs	1563 m	1565 s	I	1532 s	1555 m	1540 w
II	1492 vs	1507 vs	1502 vs	II	1505 vs	1517 vs	1517 vs
III	1465 s	1486 vs	1460 w	III	1360 w	1372 s	1375 m
IV	1395 s	1402 m	1388 m	IV	1240 m	1252 vw	1253 vw
V	1228 s	1238 vs	1266 vw	V	1206 w	1218 m	1211 w
VI	....	1148 vs,br	....	VI	....	1087 vs,br	....
VII	1128 vs	....	1135 w	VII	847 vs	855 vs	866 vs
VIII	....	1115 vs,br	....	VIII	805 vs	810 w	812 m
IX	....	1087 vs,br	....	IX	778 vs	798 vs	788 vs
X	1027 s	1040 s,br	1042 m	X	...	775 w	776 m
XI	835 vs	853 m	835 vs	XI	622 m	648 w	650 vw
XII	808 vs	840 s	795 vw	XII	...	618 s	...
XIII	773 m, sh	825 w	790 s,sh	XIII	442 m	457 w	450 vw
XIV	...	797 vs,sh	...	XIV	343 m	350 w	348 vw
XV	758 vs	792 vs	770 w,sh				
XVI	600 w	...	637 w				
XVII	...	635 m	...				
XVIII		622 s					
XIX	537 m	542 w	538 vw				

* The assignments are: s, strong; vs, very strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

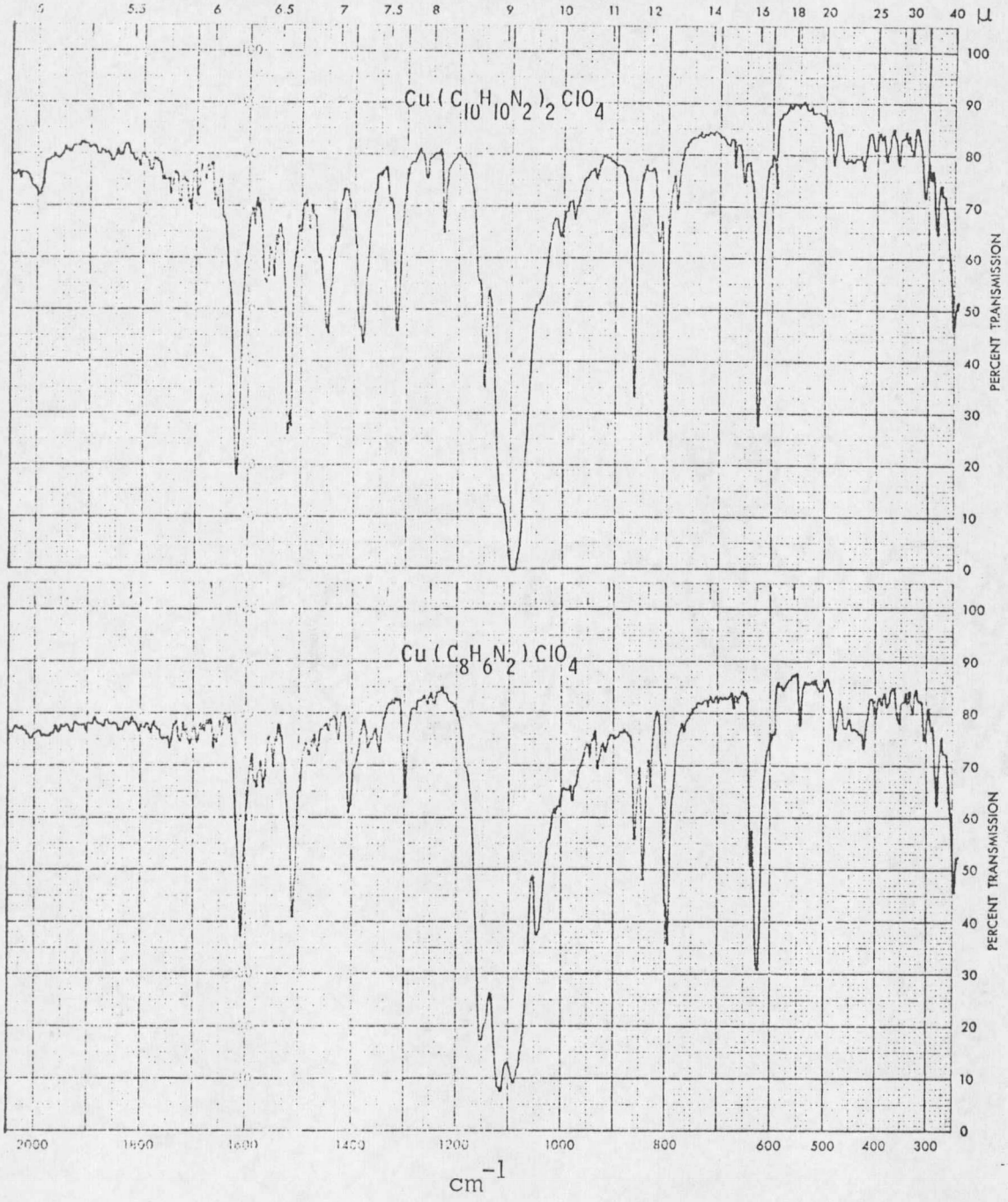


Figure 12. Infrared Spectra of $Cu(C_{10}H_{10}N_2)_2ClO_4$ and $Cu(C_8H_6N_2)ClO_4$.

oxygens). Each of the two infrared active bands is split into two components in C_{3v} symmetry and into three components in C_{2v} symmetry (8,26,60). The free perchlorate bands at about 1100 cm^{-1} and 620 cm^{-1} split into two bands resulting in four bands as observed in this compound (Figure 12). These bands indicate that the perchlorate ion is coordinated through one of the oxygen atoms to the copper atom (see Figure 12). The $Cu(NN)ClO_4$ is probably a polynuclear complex with naphthyridine molecules bridged across two copper atoms and perchlorates coordinated through one of the oxygens to the copper(I) ions. The binuclear structure shown in Figure 13 is suggested for this complex. A very similar copper(I) complex of diazoaminobenzene has been previously reported (31).

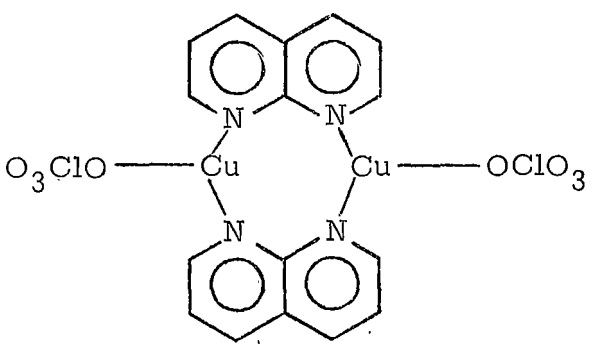


Figure 13. Suggested structure for $Cu(NN)ClO_4$ complex.

$Cu(dmNN)_2ClO_4$ and $Cu_2(dmNN)Cl_2$:— The infrared spectra of copper(I) complexes with 2,7-dimethyl-1,8-naphthyridine are listed in Table XXIII. The shifts of the ligand bands upon coordination are

similar in both $Cu(dmNN)_2ClO_4$ and $Cu_2(dmNN)Cl_2$ compounds. The splitting of the free ligand band at 1128 cm^{-1} is not observed in the spectrum of the $Cu_2(dmNN)Cl_2$. This region of the spectrum in $Cu(dmNN)_2ClO_4$ is covered by perchlorate ion bands and the ligand bands are not observable. Three very strong bands which occur at 847, 805, and 778 cm^{-1} in the free ligand spectrum are observed as two very strong and two medium and weak bands after coordination. The perchlorate anion bands in $Cu(dmNN)_2ClO_4$ occur as a broad band at 1087(vs) cm^{-1} and a sharp single band at 618(s) cm^{-1}, indicative of ionic perchlorate (7,54) (Figure 12). The ligand bands in copper(I) complexes of dmNN are similar to those of $Cu(dmNN)_2X_2$ (X= Cl or Br) in which monodentate coordination to the copper atoms was suggested. The copper-chlorine stretching frequency was not observed in the spectrum of $Cu_2(dmNN)Cl_2$.

The ultraviolet absorption bands of $Cu(dmNN)_2ClO_4$ are similar in shape to those of dmNN complexes of copper(II) ion, but different from the other copper(I) complexes in this study. There is generally a sharp increase in intensity of the ultraviolet spectrum of the copper(I) compounds, but in this compound no such increase is observed. This similarity of the ultraviolet absorption to that of mononuclear copper(II) compounds and the differences from other copper(I) compounds suggests a very different structure for this complex.

In the $Cu(dmNN)_2ClO_4$ complex the naphthyridines are coordinated through one of the nitrogens and the perchlorate anion exists as an ionic species. The stoichiometry of $Cu(dmNN)_2ClO_4$ complex is identical to the $Cu(bipy)_2ClO_4$ and $Cu(phen)_2ClO_4$ compounds (6), but coordination must be very different in the dmNN complex if the ligand is monodentate as indicated in the infrared spectrum. Thus the data available are insufficient to determine the coordinate geometry of the copper in $Cu(dmNN)_2ClO_4$. The earlier workers (7) have assigned a bidentate coordination for this same complex, erroneously reported as $Cu(dmNN)_3(ClO_4)_2$; however the positions and intensities of the bands in the region 900-700 cm^{-1} do not correspond to the bands listed for the rest of the tris compounds. This work suggests that dmNN is coordinated monodentately and the perchlorate is ionic, but is not sufficient to indicate a coordinate geometry for the copper(I) ion.

Comparison of the infrared spectrum of $Cu_2(dmNN)Cl_2$ with those of $Cu(dmNN)_2Cl_2$ and $Cu(dmNN)_2Br_2$ in which monodentate naphthyridine coordination is hypothesized shows that the spectra are very similar. This suggests that the dmNN ligand in this compound is also monodentate.

$Cu_2(NN)Cl_2$:— The infrared spectrum of the $Cu_2(NN)Cl_2$ is similar to that of $Cu(NN)_2Cl_2$ in which naphthyridines are coordinated through one of the nitrogens to the copper atom. The single band at 1136(s) cm^{-1} in the copper(II) complex appears at 1135(w) cm^{-1} in the

copper(I) compound. The very strong 835 cm^{-1} free ligand band occurs without any shift as a single sharp band and the ligand band at 760 cm^{-1} appears as a weak shoulder at 770 cm^{-1} after complexation. This indicates that naphthyridine is coordinated through one of the nitrogens to the copper(I) ion as occurs in the $Cu(NN)_2Cl_2$ complex. No bands are observed in the region 350-250 cm^{-1} which can be assigned to the copper-chlorine stretching frequency. The copper-chlorine stretching frequency of $Cu_2(CH_3N{=}NCH_3)Cl_2$ has been reported as a weak band at 311 cm^{-1} (28). The weakness of this band may account for the failure to find it in the spectrum of $Cu_2(NN)Cl_2$. The sharp melting point of the complex at $292 \pm 1^{o}C$ suggests that the complex is molecular and hence that the chlorine atoms are coordinated to the copper(I) ion.

Molecular weight determinations would be very valuable but the low solubility of the compounds did not permit molecular weight measurements.

The ultraviolet spectra of all the complexes, apart from the $Cu(dmNN)_2ClO_4$, were similar in shape, but differed from those of copper(II) compounds discussed earlier. There was a sharp increase in intensity of the spectrum with several shoulders above 36000 cm^{-1}. The band at about 38000 cm^{-1} present in copper(II) complexes (Table VII) does not appear in the $Cu_2(NN)Cl_2$, $Cu_2(dmNN)Cl_2$, and $Cu(NN)ClO_4$ complexes (Table XXIV), but since no assignment of this band has been made the significance of this absence is unclear.

Table XXIV

ULTRAVIOLET ABSORPTION SPECTRA*

λ, nm	ν, kK	ϵ_{max}, $M^{-1}K$	λ, nm	ν, kK	ϵ_{max}, $M^{-1}K$
	$Cu(NN)ClO_4$			$Cu_2(NN)Cl_2$	
307	32.6	5650	308	32.5	5750
300	33.3	6000	(302)	(33.1)	5750
(295)	(33.9)	5300	301	33.2	6100
(289)	(34.6)	4100	(295)	(33.9)	5500
(283)	(35.3)	3100	(288)	(34.7)	4200
			(284)	(35.2)	3300
	$Cu(dmNN)_2ClO_4$			$Cu_2(dmNN)Cl_2$	
315	31.8	19480	315	31.8	10500
307	32.6	17300	307	32.6	9000
302	33.1	17000	302	33.1	8800
(297)	(33.7)	12800	(296)	(33.8)	6100
(290)	(34.5)	10200	(290)	(34.5)	4700
(285)	(35.1)	8600	(283)	(35.3)	3200
250	40.0	11500			

* Parentheses represent shoulders.

The similar stoichiometry of $Cu_2(NN)Cl_2$ and $Cu_2(dmNN)Cl_2$ suggests some relation between these structures. Diazene complexes with the general formula $(RN{=}NR)Cu_2Cl_2$ have been studied previously (28). An X-ray crystallographic study of a representative compound, $(CH_3N{=}NCH_3)Cu_2Cl_2$ has shown (30) that the complex consists of infinite chains of copper and chlorine atoms (Figure 14). However the melting point of the $Cu_2(NN)Cl_2$ suggests that it is molecular and hence an infinite M-Cl-M bridged lattice seems unlikely.

Moreover a structure similar to the diazines is not possible for naphthyridine compounds. Naphthyridine is a flat rigid molecule and coordination to two adjacent chains of CuCl with naphthyridines lying in between the chains requires the sterically impossible rotation of one of the nitrogen atoms 180° around the C=C of the ring. The infrared spectra of the compounds do not indicate any bridging properties for ligands.

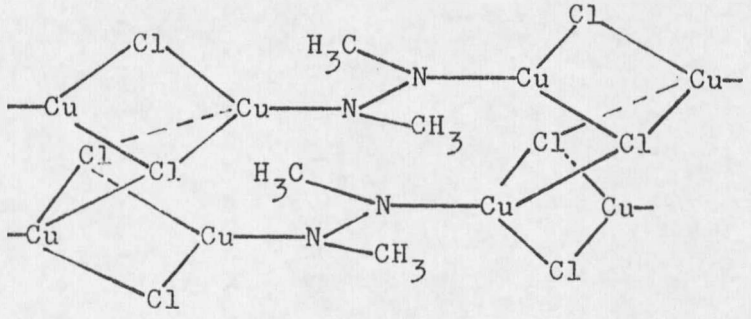


Figure 14. Structure of $(CH_3N{=}NCH_3)Cu_2Cl_2$ compound.

A structure rather different from that of the diazene is required, but there is no clear indication in the data as to the nature of this structure. This problem clearly merits further study.

SUMMARY OF PART IV.

Two copper(I) complexes of 1,8-naphthyridine, $Cu(NN)ClO_4$ and $Cu_2(NN)Cl_2$, have been synthesized. From comparisons of the data with those complexes discussed earlier, a bridged naphthyridine coordination across the two copper(I) ions in $Cu(NN)ClO_4$ with perchlorate ion being coordinated monodentately to the copper atom was found. In $Cu_2(NN)Cl_2$ complex, monodentated coordination of the ligand was suggested and a possible structural geometry was discussed.

Similarly, two copper(I) complexes of 2,7-dimethyl-1,8-naphthyridine, $Cu(dmNN)_2ClO_4$ and $Cu_2(dmNN)Cl_2$ were isolated. Monodentate coordination for the ligands was assigned. a mononuclear species for $Cu(dmNN)_2ClO_4$ and polynuclear arrangements for $Cu_2(dmNN)Cl_2$ are suggested.

APPENDIX

SULFATE AND ACETATE COMPLEXES

Several sulfate and acetate compounds of transition metal ions with 1,8-naphthyridine have been synthesized. The data on these complexes have not been analyzed, but the analytical and physical data are given in Tables XXV and XXVI respectively.

SULFATE COMPLEXES:

$Cu(NN)SO_4 \cdot 4\,H_2O$ and $Cu(NN)SO_4 \cdot 2\,H_2O$:— To a solution of 0.125 g (0.5 mmol) of $CuSO_4 \cdot 5\,H_2O$ in 10 ml of water 0.091 g (0.7 mmol) of NN was added in a Petri dish. This blue solution was kept in a closed chamber containing acetone. Upon diffusing acetone into the solution for 24 hours three different kinds of crystals were obtained. Two forms which were green and bluish-green were air stable. They were collected manually on a filter paper and were air dried. The analyses of these two forms which were separated manually showed that they had the same stoichiometry. The third form, turquoise blue, was not air stable and formed a light blue powder at room temperature. These lath-form unstable crystals were separated on a filter paper and were analyzed immediately, before decomposition could take place. The analysis showed that this unstable compound contained four molecules of hydration water, but the powder obtained after loss of water contained only two molecules of water. The weight loss in the compound, which was

determined by weighing the crystals before and after decomposition, was consistent with these determinations.

$Cu(NN)_2SO_4$:— To a solution of 0.25 g (1 mmol) of $CuSO_4 \cdot 5\,H_2O$ in 40 ml of dimethylformamide was added 3-5 drops of concentrated H_2SO_4 followed by addition of 0.26 g (2 mmol) of NN. The solution was refluxed for several minutes. This solution was filtered from the precipitate, if any, and the volume of the filtrate was reduced to about 20 ml by keeping the solution warm and under reduced pressure. The concentrated solution was kept at room temperature until crystallization was completed. The turquoise-blue precipitate was filtered and recrystallized from dimethylformamide. The crystals were washed with chloroform followed by acetone and dried over calcium chloride.

$Co(NN)SO_4 \cdot 5\,H_2O$, $Ni(NN)SO_4 \cdot 4\,H_2O$, and $Zn(NN)SO_4 \cdot 4\,H_2O$:— A solution of 0.281 g (1 mmol) of $CoSO_4 \cdot 7\,H_2O$, or 0.263 g (1 mmol) of $NiSO_4 \cdot 6\,H_2O$, and/or 0.287 g (1 mmol) of $ZnSO_4 \cdot 7\,H_2O$ in 10 ml of water containing 0.13 g (1 mmol) of NN was diffused by acetone for 24 hours. The needle-form crystals of greenish-blue nickel, pink cobalt, and white zinc complexes were isolated. The crystals were collected by filtration, washed with chloroform, and air dried. These compounds were recrystallized from their aqueous solutions by a similar method.

$Mn(NN)SO_4 \cdot 5\,H_2O$:— A solution of 0.169 g (1 mmol) of $MnSO_4 \cdot H_2O$ and 0.2 g (1.54 mmol) of NN in 15 ml of water was kept in an ice-bath for a few hours until a white precipitate was obtained. This

precipitate was collected by filtration and was recrystallized from its aqueous solution by the same procedure. The white needles were collected on a filter paper, washed with chloroform, and air dried.

$Cu(NN)SO_4 \cdot H_2O \cdot CH_3OH$:— To a solution of 0.25 g (1 mmol) of $CuSO_4 \cdot 5\,H_2O$ in 10 ml of water 0.13 g (1 mmol) of NN was added followed by addition of 30 ml of absolute methanol or methanol-chloroform mixture (3:1). Upon standing for 30 minutes the blue crystals were collected in a sintered glass funnel, washed with absolute methanol, and air dried.

$Ag_2(NN)_2SO_4$:— To a solution of 0.155 g (0.5 mmol) of Ag_2SO_4 in 70 ml of hot water 0.13 g (1 mmol) of NN in 10 ml of warm water was added. The solution was cooled slowly until crystallization was completed. The white needle-form crystals were collected by filtration, washed with water followed by acetone, and dried over calcium chloride. The recrystallization of the compound was performed from hot water.

ACETATE COMPLEXES:

$Ni(NN)_2(OAc)_2 \cdot 4\,H_2O$:— A solution of 0.245 g (1 mmol) of nickel(II) acetate tetrahydrate in 10 ml of water containing 0.26 g (2 mmol) of NN was kept at room temperature to decrease the volume of the solution to a minimum by slow evaporation. The clear green solution was kept in a chamber containing either acetone or acetone-ethylacetate

mixture. After diffusion for 24-72 hours, green well-formed crystals were collected manually, washed with chloroform, and dried over calcium chloride. The complex was recrystallized by the same procedure.

$Co(NN)_2(OAc)_2 \cdot 4\,H_2O$:— An aqueous solution of 0.249 g (1 mmol) of $Co(OAc)_2 \cdot 4\,H_2O$ and 0.26 g (2 mmol) of NN in 10 ml of water was prepared. Dark pink crystals were obtained by slow evaporation of the solution at room temperature. The well-formed crystals were collected manually on filter paper and air dried. These crystals were purified by recrystallization from aqueous solution.

$Cu(NN)_2(OAc)_2$:— To a solution of 0.4 g (2 mmol) of $Cu(OAc)_2 \cdot H_2O$ in 30 ml of warm DMF 0.52 g (4 mmol) of NN was added. This solution was kept in a desiccator containing concentrated H_2SO_4 under reduced pressure for a few days. The turquoise-blue crystals were filtered in a sintered glass funnel, washed with absolute ethanol, and dried over calcium chloride.

$Cu(NN)(OAc)_2 \cdot 2\,H_2O$:— An aqueous solution of 0.199 g (1 mmol) of $Cu(OAc)_2 \cdot H_2O$ and 0.13 g (1 mmol) of NN in 10 ml of water in a small Petri dish was kept partially covered at room temperature. The blue crystals were filtered, washed with 95% ethanol, and air dried.

Table XV

SULFATE COMPLEXES

	% Calcd.				% Found				Color	Conduct.[c] Λ(molar) cm^2 mho
	C	H	M[a]	A[b]	C	H	M	A		
$Cu(NN)SO_4 \cdot 4H_2O$			17.56	26.55	17.64		17.64	26.32	Turquoise	...
$Cu(NN)SO_4 \cdot 2H_2O$	29.54	3.09	19.50	29.49	29.81	2.87	19.42	29.35	Blue-green	6
$Cu(NN)_2SO_4$	45.79	2.88	15.13	22.88	44.88	3.01	14.96	22.94	Turquoise	7
$Cu(NN)_2SO_4 \cdot H_2O \cdot CH_3OH$	43.44	3.86	13.52	20.44	43.52	3.75	13.55	20.23	Blue	...
$Co(NN)SO_4 \cdot 5H_2O$			15.71	25.60			15.63	25.50	Pink	3
$Ni(NN)SO_4 \cdot 4H_2O$			16.45	26.91			16.26	27.07	Green	3
$Mn(NN)SO_4 \cdot 5H_2O$			14.80	25.88			14.94	25.91	White	9
$Ag_2(NN)_2SO_4$			37.71	16.79			37.56	16.83	White	53

[a] M = metal. [b] A = anion. [c] The conductivities were measured in absolute methanol.

Table XXVI

ACETATE COMPLEXES

	% Calcd.				% Found				Color	Conduct.[c] Λ(molar) cm^2 mho	Concn. $M \times 10^4$
	C	H	M[a]	A[b]	C	H	M	A			
$Cu(NN)_2(OAc)_2$			14.38	26.75			14.25	26.88	Blue	21	7.69
$Cu(NN)(OAc)_2 \cdot 2\,H_2O$			18.27	33.95			18.41	34.14	Blue	20	7.42
$Co(NN)_2(OAc)_2 \cdot 4\,H_2O$	47.16	5.15	11.17	22.39	47.57	5.14	11.24	22.69	Brownish-orange	54	7.18
$Ni(NN)_2(OAc)_2 \cdot 4\,H_2O$	47.18	5.15	11.53	23.19	47.17	5.36	11.36	23.40	Green	...	...

[a] M = metal. [b] A = anion. [c] The conductivities were obtained in absolute methanol solutions.

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